PB86-137304

Practical Guide for Ground-Water Sampling

Illinois State Water Survey Div., Champaign

Prepared for

Robert S. Kerr Environmental Research Lab.
Ada, OK

Sep 85

U.S. Department of Commerce
National Technical Information Service
NTIS

United States
Environmental Protection
Agency

Robert S. Kerr Environmental
Research Laboratory
Ada OK 74820

EPA/600/2-85/104
September 1985

PB86-137304

Research and Development

EPA

Practical Guide for Ground-Water Sampling

REPRODUCED BY
NATIONAL TECHNICAL
INFORMATION SERVICE
U.S. DEPARTMENT OF COMMERCE
SPRINGFIELD, VA. 22161

TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

1. REPORT NO.
EPA/600/2-85/104

2.

3. RECIPIENT'S ACCESSION NO.
PB86 137304/AS

4. TITLE AND SUBTITLE
PRACTICAL GUIDE FOR GROUND-WATER SAMPLING

5. REPORT DATE
September 1985

6. PERFORMING ORGANIZATION CODE

7. AUTHOR(S)
Michael J. Barcelona, James P. Gibb, John A. Helfrich and Edward E. Garske

8. PERFORMING ORGANIZATION REPORT NO.

9. PERFORMING ORGANIZATION NAME AND ADDRESS
Illinois State Water Survey
Department of Energy and Natural Resources
Champaign, IL 61820

10. PROGRAM ELEMENT NO.
CBPC1A

11. CONTRACT/GRANT NO.
CR-809966

12. SPONSORING AGENCY NAME AND ADDRESS
Robert S. Kerr Environmental Research Laboratory
Office of Research and Development
U.S. Environmental Protection Agency
Ada, Oklahoma 74820

13. TYPE OF REPORT AND PERIOD COVERED
final project report

14. SPONSORING AGENCY CODE
EPA-600/15

15. SUPPLEMENTARY NOTES
Project Officer: Marion R. Scalf, FTS 743-2308

16. ABSTRACT

This report concerns both laboratory and field testing of sampling materials and sampling mechanisms with an emphasis on minimizing error, particularly for volatile organic compound sampling and analysis. It is a companion volume to the Phase 1 report, "A Guide to the Selection of Materials for Monitoring Well Construction and Ground-Water Sampling", (EPA-600/2-83-024).

The essential elements of effective ground-water sampling include:

1. Evaluation of the hydrogeologic setting and program information needs.
2. Proper well-placement and construction.
3. Evaluation of well-performance and purging strategies.
4. Design and execution of sampling and analytical protocols which entail appropriate selection of sampling mechanisms and materials as well as sample collection, handling and analysis procedures.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group

18. DISTRIBUTION STATEMENT
RELEASE TO PUBLIC

19. SECURITY CLASS *(This Report)*
UNCLASSIFIED

20. SECURITY CLASS *(This page)*
UNCLASSIFIED

21. NO. OF PAGES
184

22. PRICE

EPA Form 2220-1 (9-73)

EPA/600/2-85/104
September 1985

PRACTICAL GUIDE FOR GROUND-WATER SAMPLING

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CR-809966-01

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DISCLAIMER

The information in this document has been funded wholly or in part by the United States Environmental Protection Agency under assistance agreement number CR-809966-01 to the Illinois State Water Survey, through the Board of Trustees of the University of Illinois. It has been subject to the Agency's peer and administrative review, and it has been approved for publication as an EPA document.

FOREWORD

The U.S. Environmental Protection Agency was established to coordinate administration of the major Federal programs designed to protect the quality of our environment.

An important part of the Agency's effort involves the search for information about environmental problems, management techniques and new technologies through which optimum use of the Nation's land and water resources can be assured and the threat pollution poses to the welfare of the American people can be minimized.

EPA's Office of Research and Development conducts this search through a nationwide network of research facilities.

As one of the facilities, the Robert S. Kerr Environmental Research Laboratory is the Agency's center of expertise for investigation of the soil and subsurface environment. Personnel at the laboratory are responsible for management of research programs to: (a) determine the fate, transport and transformation rates of pollutants in the soil, the unsaturated zone and the saturated zones of the subsurface environment; (b) define the processes to be used in characterizing the soil and subsurface environment as a receptor of pollutants; (c) develop techniques for predicting the effect of pollutants on ground water, soil and indigenous organisms; and (d) define and demonstrate the applicability and limitations of using natural processes, indigenous to the soil and subsurface environment, for the protection of this resource.

This report contributes to that knowledge which is essential in order for EPA to establish and enforce pollution control standards which are reasonable, cost effective and provide adequate environmental protection for the American public.

Clinton W. Hall

Clinton W. Hall
Director
Robert S. Kerr Environmental
Research Laboratory

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ACKNOWLEDGEMENTS

The authors appreciate the advice and support of the staffs of the USEPA R. S. Kerr Environmental Research Laboratory (Ada, OK) and the Environmental Monitoring Systems Laboratory (Las Vegas, NV). The comments and suggestions of several reviewers were very helpful in the preparation of this document. The work was also supported by the contributions of effort and time of Steven Heffelfinger, Michael O'Hearn, Mark Sievers, Pamela Beavers, and Pamela Lovett of the State Water Survey. The work has also been made possible by: the Campus Research Board of the University of Illinois, a large number of material and pump suppliers, as well as the support of our colleagues and families.

EXECUTIVE SUMMARY

Ground-water monitoring is a complex undertaking. Cost effective monitoring relies on careful planning and critical reading of the scientific literature. These activities will insure that the application of: well-placement, construction, sampling and analytical procedures, result in the collection of high quality data. The information needs of each program must be recognized and all subsequent monitoring network design and operation decisions must be made in light of the available data. In this sense, monitoring is an evolutionary process which should be refined as the information base expands.

Routine monitoring efforts may be sustained for decades. Therefore, it is unreasonable to follow preliminary guidance offered for generalized monitoring activities as the data base for a specific situation is developed. Therefore, high quality hydrologic and chemical data collected in the detection phase of monitoring are essential to planning future activities. Effective monitoring efforts are both dynamic and flexible. Our present understanding of natural and contaminated subsurface conditions is developing, but incomplete.

The practical elements of a viable long-term ground-water monitoring effort include:

Evaluation of hydrogeologic setting and program information needs

Proper well placement and construction

Evaluation of well-performance and purging strategies; and the

> Execution of effective sampling protocols which include the appropriate selection of sampling mechanisms and materials, as well as sample collection and handling procedures.

Proven ground-water monitoring procedures are in a state of rapid development at the present time. It is prudent to specify monitoring methods and results which will permit the collection of high quality, representative information for the most sensitive chemical constituents of interest. All methods used in a specific situation should be carefully documented so that one can learn as the information needs and dimensions of the monitoring effort mature.

Volatile organic compounds, redox or pH sensitive chemical constituents are problematic chemical constituents which place significant demands on monitoring efforts. It is clear that, given properly constructed and maintained sampling points, sampling and handling methods which minimize sample disturbance are the most cost-effective means available to provide high quality ground-water information. Positive displacement, no gas-contact sampling mechanisms constructed of appropriate inert materials (Teflon$^{(R)}$ > stainless steel > other plastics or ferrous materials) provide the basis for an effective monitoring effort.

Actual sampling and analytical performance (accuracy, precision, detection and quantitation limits) which ensure the collection of water originating from the formation of interest should be established in every monitoring effort, regardless of the specific information needs of individual programs. This can best be assured by the implementation of quality assurance and quality control measures which are both checked and documented carefully. The current state of our understanding of effective monitoring procedures requires that common sense also play a large part in planning ground-water sampling efforts.

If the practical recommendations of this guide are put into practice, we will have a much improved information base available in the future. This will be essential to making wise decisions on ground-water rehabilitation or other remedial actions as well as to improving our knowledge of dynamic ground-water systems.

SECTION 1
INTRODUCTION

The need for reliable ground-water sampling procedures has been recognized for years by a variety of professional, regulatory, public and private groups. The technical basis for the use of selected sampling procedures for environmental chemistry studies has been developed for surface water applications over the last four decades. However, ground-water quality monitoring programs have unique needs and goals which are fundamentally different from previous investigative activities. The reliable detection and assessment of subsurface contamination situations require that minimal disturbance of geochemical and hydrogeologic conditions occur during sampling. At this time field-proven well construction, sampling and analytical protocols for ground-water sampling have been developed for many of the more problematic chemical constituents of interest. However, the acceptance of these procedures and protocols must await more careful documentation and strong Agency recommendations for monitoring program execution. The time and expense of characterizing actual subsurface conditions places severe restraints on the methods which can be employed. Since the technical basis for documented, reliable drilling, sample collection and handling procedures is in the early stages of development, conscientious efforts to document method performance under real conditions should be a part of any ground-water investigation.

This guide provides the elements of effective ground-water sampling for routine applications. This is not to minimize the ongoing development of specific sampling or in situ sample collection methods for research purposes. It is important, however, that essential elements of reliable sample collection and handling are understood so that the eventual development and application of more sophisticated methods can be based on high quality data.

We proceed from the point of view that the placement of wells for sampling access has been done appropriately and the task at hand is to construct the wells and to collect water samples representative of the formation of interest. The sampling procedures described in this guide are recommended on the basis of long-term reliability in routine monitoring programs.

LITERATURE OVERVIEW

Much of the literature on routine ground-water monitoring methodology has been published in the last ten years. The bulk of this work has emphasized ambient resource or contaminant source monitoring rather than case-preparation or enforcement efforts. General references which are useful to the design and execution of sampling efforts are those of the U.S. Geological Survey (1,2), the U.S. Environmental Protection Agency (3,4,5,6) and those of a number of other groups (7,8,9). In large part, these past works treat sampling in the context of overall monitoring programs providing descriptions of available sampling mechanisms, sample collection and handling procedures. The impact of specific methodologies on the usefulness or reliability of the resulting data have received relatively little discussion (10,11).

Routine monitoring data is used most often to determine if any deterioration in water quality has occurred over time. In principle, this information will accurately represent hydrogeologic or geochemical conditions at a site and enable an understanding of the dynamics of subsurface systems. A certain level of knowledge must be achieved to insure the success of a detective monitoring program and to plan modifications or refinements of the monitoring program if contamination is indicated. Otherwise, poor decisions may result which will prove to be far more expensive and time-consuming than the careful performance of proper detective monitoring activities would have been.

High-quality chemical data collection is essential in ground-water monitoring programs. The technical difficulties involved in representative sampling have been recognized only recently (10,12). It is clear that the long-term collection of high quality ground-water chemistry data is more involved than merely selecting a sampling mechanism and agreeing on sample handling procedures. Efforts to detect and assess contamination can be extremely unrewarding without accurate (e.g. unbiased) and precise (e.g. comparable and complete) concentration data on ground-water chemical constituents.

Gillham et al. (13) have published a very useful reference on the principal sources of bias and imprecision in ground-water monitoring efforts. Their treatment is extensive and stresses the minimization of random error which can enter into well-construction, sample collection and sample handling operations. They further stress the importance of collecting precise data over time to maximize the effectiveness of trend analysis, particularly for regulatory purposes. Accuracy is also very important, since the ultimate reliability of statistical comparisons of results from different wells (e.g. upgradient versus downgradient samples) may depend on differences between mean values for selected constituents from relatively small replicate sample sets.

GROUND-WATER SAMPLING AND QUALITY ASSURANCE

Individual ground-water sampling and analytical events yield results which provide a snapshot picture of hydrogeologic and chemical conditions at a monitoring site. When the results of successive events are assembled properly, they enable one to better understand the nature, extent and degree of subsurface contamination. It is important to remember that hydrologic and chemical conditions vary in both time and space and that the subsurface environment of ground water is dynamic. Therefore, sampling frequency and the location of discrete sampling points must be considered carefully to resolve the temporal and spatial distributions of ground-water contaminants.

Each ground-water sample must be collected so as to insure the reliability of analytical determinations. Also, accurate and precise measurements of water level and hydraulic conductivity must be made so that the analytical results can be interpreted with consideration of the hydrogeologic system.

Achieving the information needs of a ground-water sampling program over a specified time period requires careful planning and execution of the sampling design. Careful planning is particularly crucial to distinguishing between the actual hydrologic and chemical variability at a site and that which may arise from errors in the sample collection, handling, and analysis procedures. Each field measurement and water sample collected for laboratory analysis should also be representative of the discrete sampling point within the sampling network. Emphases are often placed on quality control and quality assurance for chemical analysis alone. One should keep in mind that there is no substitute for high quality sampling and field measurements.

A high quality set of hydrologic and chemical data is accurate, precise, comparable, and complete. Also, data must be collected at a minimum level of sensitivity and completeness to satisfy the information needs of the sampling program. Accuracy, precision, sensitivity, and completeness are measures of sampling and analytical performance. The accuracy of each concentration datum is the measure of its closeness to the true value. Accuracy is normally expressed as an average of a number of measurements to the true value. The accuracy of analytical procedures may be assessed by the use of standard reference materials. In this case, accuracy is expressed as the percentage of the ratio of the measured value to the true value. For environmental samples, where the true value is frequently unknown, accuracy is reported as bias (or the percent recovery minus 100) established by internal or surrogate standard techniques. Generally, values of bias in excess of ±20% indicate systematic error or a problem with sampling or analytical procedures.

The precision of a data set is a measure of the probability that a measurement will fall within certain confidence limits. Precision is frequently expressed as the standard error ($s_{\bar{x}}$) of the mean value ($\bar{x}$) of a set of replicate determinations (n) at a stated mean (or true) value. The standard error is related to the standard deviation (s) by the expression: $s_{\bar{x}} = s \div \sqrt{n}$. Increasing the number of replicates at an established level of precision will generally improve the level of confidence (reduce random error) in the data. Duplicate sample values which differ by less than ±50% relative difference indicate good error control.

Sensitivity is a term which relates to both the limit of detection (LOD) and the method detection limit for a particular chemical constituent. The method detection limit pertains to the lowest concentration of a particular chemical constituent which can be measured reliably in a sample. The LOD is the lowest concentration level which can be determined to be statistically different from a blank. A practical guideline is to set the LOD for a specific constituent at a level equivalent to three standard deviations (expressed in mass or concentration) above the blank. This level establishes a threshold for qualitative or "trace" detection sensitivity and provides a degree of confidence in values reported as "less than" a detectable concentration. More stringent criteria for quantitation set the limit of quantitation (LOQ) at 5 or 10 standard deviations above the blank to insure that quantitation is on a sound foundation. Regardless of the convention used, it is important that the LOD and LOQ be reported with all data sets at least for certain problematic chemical constituents. Completeness of the total planned data set should include the performance parameters defined above. Sampling and analysis procedures contribute to the overall quality of the data set and documentation of control over both systematic and random error is central to the effort.

The crucial elements of planning a ground-water sampling effort are discussed in detail in this guide. High quality data collection requires strict adherence to proven well construction, sampling and analytical protocols developed with due precautions against bias, imprecision, contamination or chemical alteration of the water sample. In this respect all field measurements attendant to water sample collection are considered part of the sampling protocol. Quality control procedures built into sampling and analytical protocols will guard against the loss of data by minimizing both systematic and random error.

ELEMENTS OF THE QUALITY ASSURANCE PROGRAM

A quality assurance (QA) program is a system of documented checks which validate the reliability of a data set. QA procedures are used to verify that field and laboratory measurement systems operate within acceptable limits. These limits should be determined during sampling program design for each measurement which the program requires. The limits may be modified or refined as new information is gathered. However, a documented basis for evaluating the need for modification must be established if the expense and manpower involved in ground-water investigations is to yield cost-effective, high quality data.

The QA program should be implemented as a set of basic measurement procedures and corresponding quality control checks (6). The overall effectiveness of the quality control checks in reducing errors should be audited by a person or technique outside of the normal sampling and analytical operations. In this way the QA program will ensure that quality control (QC) procedures are followed on a daily basis to: reduce variability and errors, identify and correct measurement problems, and provide a documented statistical measure of data quality. The effectiveness of the overall program demands that all personnel are aware of the QA/QC requirements for the investigation and that the quality control objectives are understood.

OBJECTIVES

Sampling Quality Control

An understanding of the specific characteristics of the study site is required to plan effective QC checks. Generally, this understanding is achieved in phases which must be recognized by the sampling program manager. Each sampling datum represents a single opportunity to collect data from a sampling point which can rarely be retrieved if errors are not identified.

A minimal data set consisting of selected field measurements and sample volume recovery must be agreed upon to comprise a "sample." Then a minimum completeness or data recovery level should be defined which will adequately characterize existing conditions and fall within expected limits of future variability.

It must be kept in mind that even with adequate QA auditing of sample results within control limits, there are system constraints on the subsequent interpretation of sampling and analytical information. Hydraulic and hydrologic properties are, to some extent, scale dependent and ground-water monitoring is frequently conducted in geologic formations which are not aquifers. Further, solution chemical properties are only part of the subsurface geochemical system. These and other unique characteristics of ground-water systems may introduce systematic error or bias into monitoring data sets. Gillham et al. (13) have addressed many of these potential problems.

Effective QC procedures for ground-water sampling should be based on proven field measurement and sampling procedures. The wide variety of hydrogeologic and geochemical conditions of interest for contaminant monitoring have been investigated by an equally diverse combination of procedures. Very few of these procedures have been standardized after systematic development and controlled evaluation trials. Therefore, tailoring QC procedures to the situation at hand is a complex task. Well construction and development techniques as well as sampling procedures, mechanisms, and materials all have the potential to introduce errors into monitoring results. These sources of error should be considered in the development of QC checks.

Given that the ground water may be under relatively high partial pressures of nitrogen or carbon dioxide, water samples need to be handled very carefully. The samples also originate in geologic media which are rarely isotropic at the regional to local scale. Frequently, suspended solids accompany water sample collection which can seriously affect analytical results. The discussions provided by Sisk (6) and Brown and Black (14) are useful in planning general QC procedures for ground-water sampling efforts.

A common challenge to effective ground-water data quality control is that the accuracy of a sample result is difficult to judge, since the true value is unknown. Accuracy of individual measurements must therefore be judged by the analysis of a reference material or by spiking the sample with a known quantity of analyte followed by reanalysis. The results from field blanks and standards may then be compared to the results of laboratory standards and spiked samples to gain confidence in the accuracy of sample analyses. The precision of measurements within a data set is thus defined as the average agreement between repeated measurements on samples and standards. Quality control over the first four steps involved in sample access and retrieval is difficult to achieve. This is shown schematically in Figure 1.1. Therefore, it is

Step	Sources of Error
In-Situ Condition	
Establishing a Sampling Point	Improper well construction/ placement; inappropriate materials selection
Field Measurements	Instrument malfunction; operator error
Sample Collection	Sampling mechanism bias; operator error
Sample Delivery/Transfer	Sampling mechanism bias; sample exposure, degassing, oxygenation; field conditions
Field Blanks, Standards	Operator error; matrix interferences
Field Determinations	Instrument malfunction; operator error; field conditions
Preservation/Storage	Matrix interferences; handling/labeling errors
Transportation	Delay; sample loss

Figure 1.1. Steps in ground-water sampling and sources of error

very important to choose well construction and sampling protocols which are simple and minimize disturbance in order to collect accurate data.

One can readily observe that the integrity of both the sampling point and sampling mechanism are as critical as operator expertise to minimize the error or variance introduced into the sample results. Decisions made in establishing a sampling point and the choice of sampling mechanisms can introduce significant systematic error (bias) into all subsequent sample results which may go undetected without careful QA auditing of the data as soon as possible. Further, documented sampling QC checks and QA audits are controlling factors in the usefulness of the analytical data. The laboratory can only be expected to reliably report data based on the samples, field standards, and blanks as received.

The potential sources of error noted in Figure 1.1 define essential elements of sampling quality control. These are:

1) Proper calibration of all sampling and field measurement equipment
2) Assurance of representative sampling, particularly with respect to site selection, sampling frequency, well purging and sample collection
3) Use of proper sample handling precautions

Analytical Quality Control

Laboratory quality control is necessary to ensure valid analytical results. Analytical QC procedures must be developed in parallel with those involved in the sampling operation. Whether the laboratory analyses are made by an in-house or contract lab, the value of blind control samples and blanks submitted as "normal" samples is enormous. Blind control samples may be prepared solutions or ground water spiked with the contaminants of interest at known concentrations. Blind controls provide the only true check on the accuracy of analytical results. Effective QC procedures provide daily checks that the analytical system is in statistical control. Blind control samples and multiple determinations should be emphasized wherever possible. Repeat sampling and analysis is a poor second choice to performing the tasks adequately in the first place. The variables involved in sampling must be controlled to the maximum extent possible for the rigors of laboratory QC procedures to be meaningful. Three useful references for planning QA and QC for ground-water data collection are contained in reviews by Nacht (15) and Keith et al. (16), and Kirchmer (17,18).

The need to establish a measure of confidence in the analytical results is underscored in a formal laboratory QA program. The program should address three main functions: the control, determination and documentation of data quality. These are minimal criteria for effective laboratory QC, which should extend to field determinations. Regardless of the analytes of interest and the degree of sensitivity required by the information needs of the ground-water sampling program, every laboratory should adhere to well-documented control procedures. These procedures have been reviewed in general by Dressman (19) and Dux (20). The expectations which may be anticipated from contract laboratory services are no less rigorous than those of in-house laboratories. Specifics of such cooperative sampling/analytical arrangements have been covered by Kingsley et al. (21) and Kingsley (22).

In contrast to the steps in the sampling protocol, analytical quality control is straightforward, provided that the analytical laboratory staff is made aware of any unusual attributes of the samples. This type of feedback can substantially improve the validity and interpretive value of measurement results.

The steps of an analytical protocol are normally quite specific to the individual analytes of interest. The planning of comprehensive QA procedures should be done carefully with each individual step in the analytical protocol taken into account. In general, the analytical protocol can be depicted as shown below in Figure 1.2. Appropriate QA audits of the QC measures at each step should serve to keep potential analytical errors in control.

Instrument malfunctions, analyst errors, and the use of "aged", old or deteriorated standards pose problems that can be detected and corrected with good QA/QC procedures. More difficult obstacles arise from the application of "standard" methods to the analysis of highly contaminated samples. Matrix or direct interferences are among the most difficult sources of error to bring under control (23). Thoroughgoing QC requires that standard methods be validated for the most difficult sample matrix encountered within a particular set of samples. Validation by internal standardization techniques should be done over the entire range of concentration represented in the sample results (24,25).

The necessary elements of an effective laboratory QA program are:

1) Adherence to documented laboratory QC procedures, including: proper calibration of instrumentation, verification of daily standardization and analytical performance parameters (accuracy and precision) for all procedures, daily analysis

Step	Sources of Error
Samples, from Storage Field Blanks and Standards	"Aged" samples; loss of analytes; contamination
Subsampling	Sample aging/contamination in lab; cross-contamination; mishandling/labeling
Procedural Standards	"Aged" standards; analyst error
Analytical Separation	Matrix interferences; inappropriate/invalid methodology; instrumental malfunction/analyst error
Analysis	Matrix interference; inappropriate/invalid methodology; instrumental malfunction/analyst error
Reference Standards	"Aged" standards
Calculations	Transcription/machine errors; sample loss in tracking system; improper extrapolation/interpolation; over-reporting/under-reporting errors
Results	

Figure 1.2. Steps in water sample analysis and sources of error

of sample replicates, standards, spiked samples and blanks by approved methodologies and the use of QC charts to document the validity of laboratory results

2) Participation in round-robin or interlaboratory studies
3) Prompt recording, storage and retrieval of laboratory results with the corresponding analytical performance parameters

The development of a total QA/QC program for ground-water sampling and analysis must be approached carefully. The care exercised in well placement and construction, and sample collection and analysis, however, can pay real dividends in the control of systematic errors. Repeated sampling and field measurements will minimize the effect of random errors induced by field conditions or system malfunction.

The responsibility for the selection of reliable sampling and analytical methods is to some extent shared by the sampling program director and the client or agency in need of the information. As more high quality data become available, QA/QC planning will be facilitated for environmental sampling programs. The American Chemical Society Committee on Environmental Improvement has published a valuable reference for reporting data quality (e.g. accuracy, precision, LOD, LOQ, sensitivity) in a consistent format for monitoring purposes (26). This guide contains recommendations based on experience and published results. It will be revised and modified accordingly as the information base grows. Therefore, it should be used in conjunction with the future amendments of existing standard procedural documents (27,28,29).

REPRESENTATIVE GROUND-WATER SAMPLING

Representative sampling is probably most difficult in situations where reliable data is needed most (30). Chemists have struggled for decades with the difficulties involved in obtaining representative analytical results from bulk solid or natural water samples. Scientists who have worked with environmental samples fully appreciate these difficulties. Statisticians, on the other hand, hold exact views concerning the characteristics of representative samples. Statistically, a representative sample is a subset of a set (or universe called the population) which has the average characteristics of the set. For ground-water samples, one must assume that such a sample is representative of the aquifer or geologic formation from which it came. It follows then that the results of representative sampling and controlled analytical determinations provide an accurate measure of the *in situ* condition at the time of sampling. Claassen (31) has demonstrated that *an approximation* of the *representativeness of a ground-water sample alone* is achievable given the complexities and costs involved in exhaustive investigations of the subsurface. Verification of the extent of representativeness is thus the responsibility of project staff.

The goal of representative sampling is a relatively straightforward undertaking in materials' analysis or investigations of well-mixed homogenous surface-water bodies. Sources of error or variance in sampling or analysis should be independently verifiable if the measurement systems are in statistical control. This is possible if truly random sampling can be conducted and invalid samples can be identified through the use of controls and blanks.

Representative ground-water sampling, however, is limited to replicate discrete samples from established sampling points which may accurately and precisely reflect the average properties of the measured system. Sampling accuracy, however, cannot be unequivocally verified in the field. It is vitally important that the limits of the measured system are understood by the project personnel responsible for the interpretation of the data (12). In this way, the interpretation of "high" or "background" levels of specific chemical constituents will be consistent with the hydrogeologic system description. Statistical theory and manipulations applied to data on hydrogeologic or geochemical systems cannot substitute for expert judgment.

Claassen (31) pointed out that there exists a marked scale dependency of the heterogeneity of aquifer systems. He suggested that most aquifers are microscopically (~100 μm) heterogenous, some are homogenous on a somewhat larger scale, while all are probably heterogenous on a regional scale (km). His publication details suggested guidelines for evaluating aquifer representation which should be carefully considered in planning ground-water investigations of all types. Data requirements for water source definition and aquifer representation of ground-water samples are listed in Table 1.1. This data should be recorded for each sampling point and updated after each scheduled well maintenance (e.g. redevelopment operation). The well pumping history, in particular, should be updated on each sampling date to insure that any deterioration in well performance can be fully documented.

Hydrologists and geochemists have made progress towards the resolution of these problems of scale for aquifer representation. The work of Ingamells (32) and Ingamells and Switzer (33) is notable in this area of

Table 1.1. Data Requirements for Water-Source Definition and Aquifer Representation of Ground-Water Samples (Modified after Claassen, reference 31)

A. Drilling history

1. Well depth and diameter
2. Drill-bit type and circulating fluid
3. Lithologic data from cores or cuttings
4. Well-development before casing
5. Geophysical logs obtained

B. Well-completion data

1. Casing sizes, depths and leveling information relative to both land surface and top of casing
2. Casing material(s)
3. Cemented or grouted intervals and materials used
4. Plugs, stabilizers, and so forth, left in hole and materials used
5. Gravel packing: volume, sizes, and type of material
6. Screened, perforated, or milled casing or other intervals which allow water to enter the borehole
7. Pump type, setting, intake location, construction materials, and pump-column type and diameter
8. Well maintenance record detailing type of treatment and efficiency

C. Well pumping history

1. Rate
2. Frequency
3. Static and pumping water levels

D. Estimation of effect of contaminants introduced into aquifer during well drilling and completion on native water quality

E. Effect of sampling mechanism and materials on the composition of ground-water sample

1. Addition of contaminants
2. Removal of constituents
    a. Sorption
    b. Precipitation
    c. Degassing

research, however its practical application to hydrogeologic problems has been limited. An inventive technique for resolving scale and heterogeneity problems in aquifer representation has been reported by Keely (34). Briefly, a combination of pumped wells or pumping wells and monitoring wells are sampled over a time series simultaneous with water level and yield measurements. The combined chemical time series samples and the drawdown results provide a data set which describes the spatial variability of dissolved chemical constituents, as well as aquifer transmissivity and storage values. The application of this technique to a contamination problem in Washington State yielded encouragement for its use and refinement for future work (35). Multi-level sampling point arrays also hold promise for the resolution of scale problems. However, most of the published reports are limited to demonstrations of techniques (36,37,38). Systematic evaluations of the performance of sampling protocols for chemical constituents are rare.

Criteria for Documenting Representative Sampling

It should be evident that representative sampling in the strict statistical sense is a challenging undertaking. To some extent the criteria for "representativeness" depend on the level of detail required in the program. The requirements for documenting representative samples from the measured system will vary from site to site and perhaps from sampling point to sampling point, depending on the situation under investigation. This document defines representative sampling *a priori* as representative for the specific purposes of the ground-water investigation. In the case of regulatory compliance studies, the criterion for representativeness may be that which will be considered by the appropriate agency to be representative of the regulated facility. For example, charge balance considerations and minimum acceptable accuracy and precision limits for the determination of the contaminants of interest are useful criteria for representative samples.

There are two sets of essential requirements for representative sampling. The first set of criteria must be based on some knowledge of the measured system and the experience of project planning staff. Close attention must be paid to the requirements listed in Table 1.1, as well as the potential impacts of: well placement, sampling frequency, the mobility and persistence of chemical constituents and natural sources of variability in the hydrogeology and geochemical characteristics of the site. These criteria are subjective to some extent and evaluation of a data set's "representativeness" may only be possible after extensive preliminary investigation. As the level of detail involved in a sampling program increases, one must be careful to avoid excesses in borings for core collection or well installation. Every disturbance of the subsurface has the potential to contribute to contaminate migration and confound data interpretation. Good detective work on site characteristics and operational history can minimize the cost and disturbance of extensive sampling activities.

The second set of criteria addresses the details of the sampling and analytical protocols. They are based on the assumption that a properly designed and executed ground-water sampling plan will enable documented evaluation of the significance of the sample mean and the variation between the mean and other members of the set. Basically, reliable protocols provide a known level of confidence in the representativeness of the sample.

Accuracy, Precision, Detection/Quantitation Limits and Completeness

The critical performance parameters common to both the sampling and analytical protocols are accuracy, precision, minimum detection limits and completeness. Proper planning of a comprehensive sampling program, which includes QC check and QA auditing procedures to insure high quality results, requires that each step in the protocols is evaluated for each of the performance parameters. The most direct way to meet this requirement is to specify and document the sampling protocol for the most sampling error prone class of chemical constituents of interest. In each class, certain constituents may require refinement of the protocol for reliable sampling. Detailed documentation of accuracy, precision and minimum detection limits for the corresponding analytical procedures should be provided as well. In this manner sampling errors can be evaluated independently from those involved in the analytical work.

Establishing the performance of the sampling protocol to achieve error control requires the execution of a controlled sampling experiment. If possible, one should seek to verify sampling accuracy and precision over the potential concentration range of the most sensitive chemical constituent of interest. This type of experiment could establish the lowest practical level of a chemical constituent which can be sampled within certain accuracy and precision limits. This minimum "collectable" concentration would correspond to the LOQ for analytical operations. However, sampling accuracy cannot be verified in the field, since the "true" or in situ value is unknown and it is most unlikely that any single (or average) value for a particular chemical constituent could be considered as the "true" even for very localized sites. Therefore, the accuracy of the sample retrieval and collection steps, which involve both the sampling mechanism and materials, must be evaluated in controlled laboratory experiments. These experiments should simulate field conditions and maintain a known concentration source of the most sensitive chemical constituent of interest. Precision, on the other hand, can be evaluated in the field or the laboratory if a sufficient number of replicate determinations can be performed.

There have been few controlled sampling experiments reported which provide supporting data for the evaluation of representative sampling performance. Field experiments have been limited to documenting apparent discrepancies in accuracy by different sampling techniques (11,39), or studies which establish the precision of developing sampling techniques (40). Since it is extremely difficult to maintain control over sampling performance which may be largely operator dependent, the choice of a specific sampling mechanism must be made very carefully. If a sampling mechanism is chosen which has not been subjected to controlled performance testing, the user should provide documentation which assures control over mechanism related error. It may be that evaluations of the accuracy of sampling mechanisms must be inferred by comparisons with published data and the precision should be established for each study with a well designed sampling experiment. Thorough consideration must be given to sources of systematic (bias) and random (imprecision) error at each step in the sampling protocol. The sampling mechanism is of particular importance in this regard as it largely determines the complexity of the sampling protocol.

SECTION 2

ESSENTIAL ELEMENTS OF A GROUND-WATER SAMPLING PROGRAM

The technical literature on ground-water sampling provides a great deal of information on selected aspects of an efficient sampling program. However, valid data on reliable methods for drilling, well completion/development, and sampling reactive or organic chemical constituents in ground water are scarce.

Recommendations for conducting ground-water sampling programs stress the use of "appropriate" drilling and sampling methods or material's choices which will permit the collection of representative samples. This leaves many critical decisions open to discretion when data on the hydrogeologic setting or dissolved chemical constituents may be incomplete. This section provides specific recommendations for establishing a sampling point and conducting a sampling effort which should be sufficient to the needs of most routine ground-water investigations. In many cases, the detail and precautions which must be considered in planning a representative sampling effort cannot be predicted until a substantial amount of high quality data is made available by preliminary sampling.

Due care to insure the collection of unbiased, precise hydrologic and chemical data should be exercised from the outset in all monitoring efforts. The data set should then be subjected to constant scrutiny and reevaluation as the situation becomes better defined. This approach is logical and cost-effective. Poorly conceived or "cook-book" sampling programs will ultimately end up generating poor data at considerable long-term expense. The logical, phased approach also facilitates regulatory review of the data and decision-making for assessment or remedial actions.

HYDROGEOLOGIC SETTING AND SAMPLING FREQUENCY

The hydrogeologic conditions at each site to be monitored must be evaluated for the potential impacts the setting may have on the development of the monitoring program and the quality of the resulting data (41). The types and distribution of geologic materials, the occurrence and movement of ground water through those materials, the location of the site in the regional ground-water flow system, the relative permeability of the materials, as well as potential interactions between contaminants and the geochemical and biological constituents of the formation(s) of interest must all be considered.

Hydrogeologic Setting

There are three basic types of geologic materials normally encountered in ground-water monitoring programs. These are: 1) porous media; 2) fractured media; and 3) fractured porous media. In porous media, the water and contaminants move through the pore spaces between individual grains of the media. These media include sand and gravels, silt, loess, clay, till, and sandstone. In fractured media, the water and contaminants move through cracks or solution crevices in otherwise relatively impermeable rock. These media include dolomites, some shales, granites, and crystalline rocks. In fractured porous media, the water and contaminants move through both the intergranular pore spaces as well as cracks or crevices in the rock or soil. The occurrence and movement of water through the pores and cracks or solution crevices depends on the relative porosity and degree of channeling from cracks or crevices. These media include fractured tills, fractured sandstone, and some fractured shales. Figure 2.1 illustrates the occurrence and movement of water and contaminants in these three types of geologic materials.

The distribution of these three basic types of geologic materials is seldom homogeneous or uniform. In most settings, two or more types of materials will be present. Even for one type of material at a given site, large differences in hydrologic characteristics may be encountered. The heterogeneity of the materials can play a significant role in the rates of both tracer and contaminant transport, as well as the optimum strategy for monitoring a site.

Once the geologic setting is understood, the site hydrology must be evaluated. The location of the site within the regional ground-water flow system also must be determined. Piezometric surface data or water level information of each geologic formation at properly selected vertical and horizontal locations is needed to determine the horizontal and vertical ground-water flow paths at the site of interest. Figures 2.2 and 2.3 illustrate two geohydrologic settings commonly encountered in eastern regions of the United States where ground-water recharge exceeds evapotranspirational rates. Figure 2.4 illustrates a common geohydrologic setting for the arid western regions of the United States.

In addition to determining the directions of ground-water flow, it is essential to determine the approximate rates of ground-water movement to properly design a monitoring program. Hydraulic conductivity and gradient data are required to estimate the Darcian or bulk flow rates of ground water. Hydraulic conductivity data should be determined using

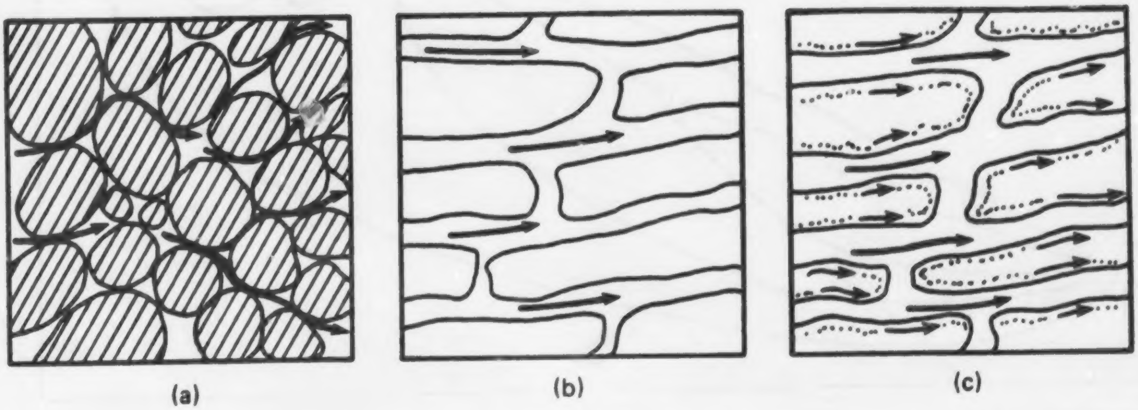


Figure 2.1. Occurrence and movement of ground water through a) porous media, b) fractured or creviced media, c) fractured porous media

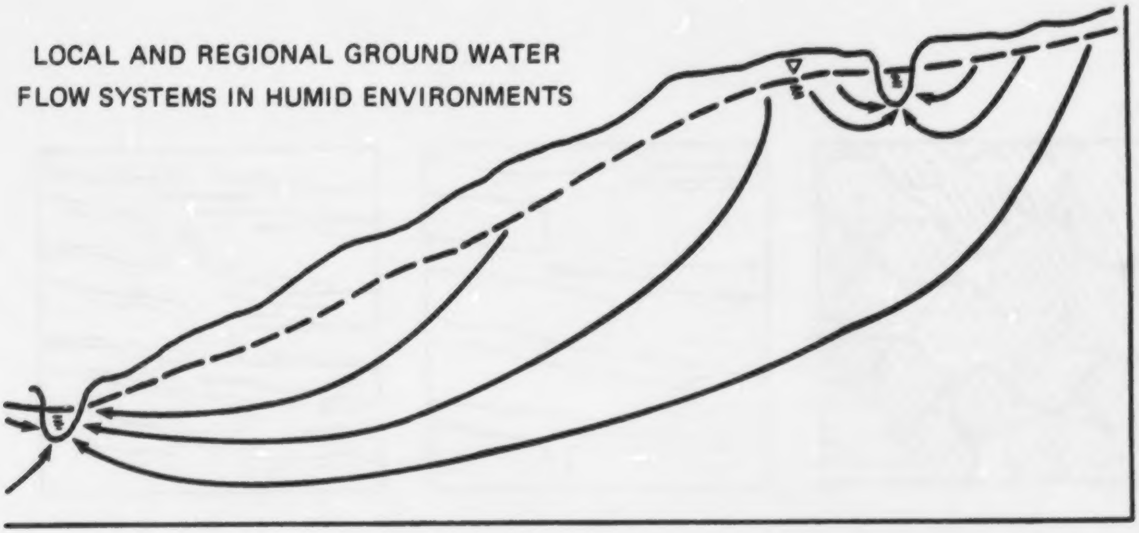

LOCAL AND REGIONAL GROUND WATER
FLOW SYSTEMS IN HUMID ENVIRONMENTS

Figure 2.2

TEMPORARY REVERSAL OF GROUND-WATER FLOW DUE TO FLOODING OF A RIVER OR STREAM

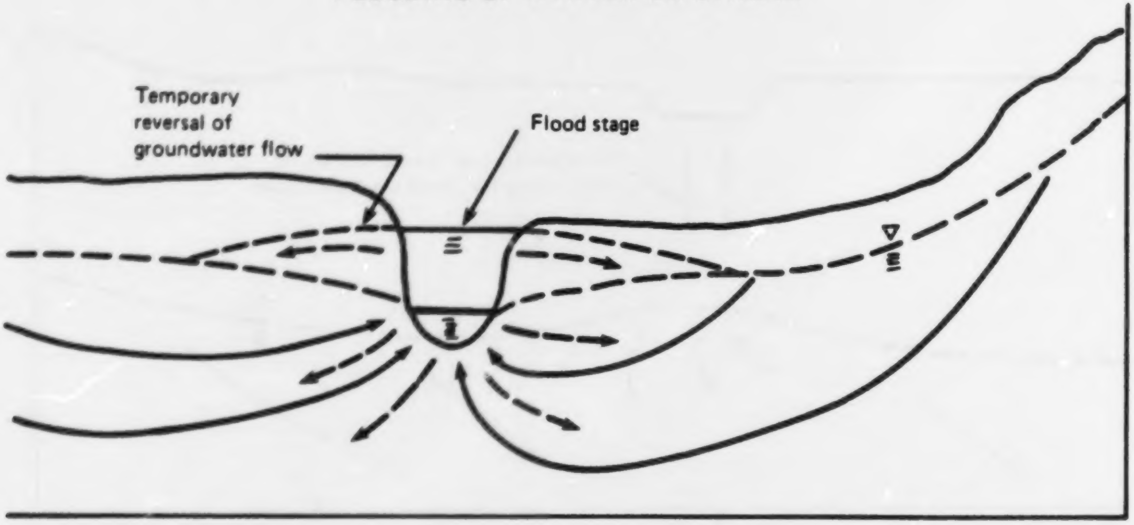
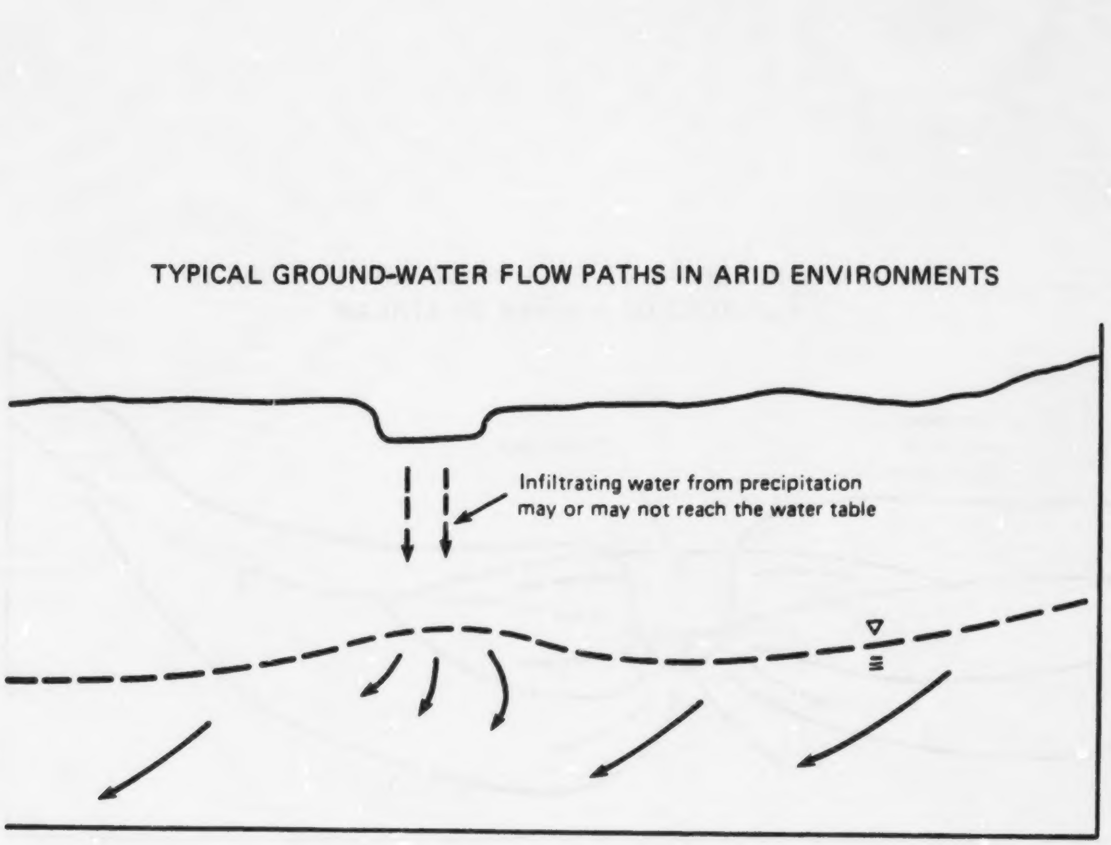

Temporary reversal of groundwater flow
Flood stage

Figure 2.3


TYPICAL GROUND-WATER FLOW PATHS IN ARID ENVIRONMENTS

Infiltrating water from precipitation may or may not reach the water table

Figure 2.4

slug or pump test data from field tests. Hydraulic conductivities determined in the laboratory have been shown to vary by orders of magnitude from values determined by field methods. Determining the hydraulic conductivity of materials tapped by individual wells also provides data on the relative heterogeneity of the materials in question.

To determine the actual or linear flow velocities, the effective (or dynamic) porosity of the materials should be determined. The effective porosity of geologic materials is a factor which influences the materials' ability to transmit water. All of the pore spaces within geologic materials are not available for water or solute flow. Dead end pores and the portion of the total porosity occupied by water held to soil particles by surface tension forces do not participate in the transport of ground water or solutes. Methods for measuring effective porosity are being developed currently. In the absence of measured values, drainable porosity is often used to approximate effective porosity. Figure 2.5 illustrates representative values of drainable porosity and total porosity as a function of aquifer particle size.

Knowledge of the rates of ground-water flow is essential to determine if the locations of the monitoring wells are within reasonable flow distances of the potential sources of pollution. Similarly, rate of travel data can be used to calculate reasonable sampling frequencies. This could be particularly important in attempting to monitor the potential migration of a spill or intermittent pollution source.

Finally, the geochemical and biological properties of the aquifer matrix should be evaluated in terms of their potential interference with the goals of the monitoring program. For example, chemical reactions or biological transformations of target chemical species may introduce

TOTAL POROSITY AND DRAINABLE POROSITY FOR TYPICAL GEOLOGIC MATERIALS (After Todd, 1980)

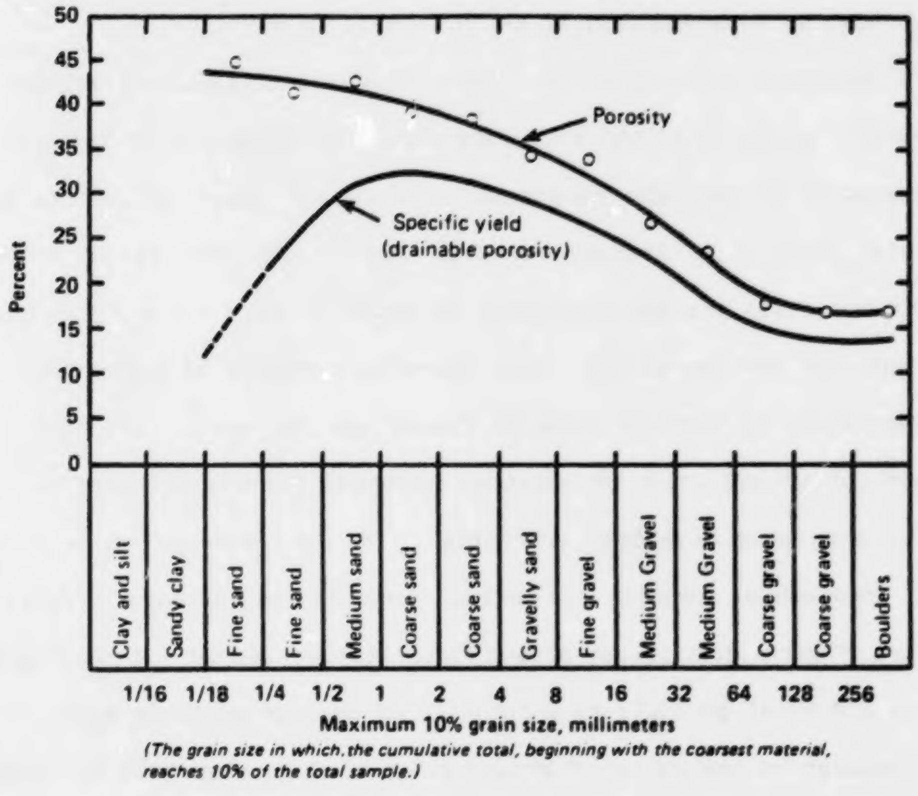


Figure 2.5

artefacts into the results. Physical and hydrologic conditions will determine whether or not evidence for chemical or biological interactions can be collected. If the potential for these reactions or transformations exist, consideration should be given to screening for likely intermediates or transformation products.

The importance of understanding the hydrogeologic setting of the site to be monitored cannot be overemphasized in developing an effective sampling program. Similarly, the effects of the hydrogeologic setting on the samples to be collected should be evaluated in detail and considered in developing the sampling protocol.

Sampling Frequency

Traditional determinations of optimum frequencies for ground-water sampling have been made by regulation or from statistical arguments in analogy with surface water monitoring experiences (43,44). Sampling frequencies determined by these methods emphasize data needs and the economics of sample collection and analysis. A more reasoned approach is to first evaluate the type of source that is being monitored, a spill, slug, intermittent, or continuous source. Then one should consider the likely pulse or continuous plumes of contaminants to be monitored; determine the minimum desired sampling frequency in terms of length along the ground-water flow path and use hydrologic data to calculate the required frequency to satisfy these goals.

The type of potential pollution source has a direct influence on the resulting plume that may be created. In the case of a spill or slug source of pollution, discrete plumes may result. The size, shape, and rate of plume movements will be dependent on: source characteristics, the hydrologic and geologic nature of the site in question and the chemical reactivity and biological interaction of individual contaminants with the subsurface environment. Figure 2.6a illustrates this type of phenomena. Intermittent releases of a pollutant may result in a series of discrete plumes that may or may not overlap depending on the relative frequency of the releases and the factors mentioned above. Figure 2.6b illustrates this type of phenomena.

Continuous sources of pollution result in the development of plumes that may approach steady state conditions for nonreactive conservative chemical species. The size and shape of this type of plume can be estimated using a relationship described by Todd (42). Todd analyzed the effects of regional ground-water flow on the circular cone of depression in the water surface developed by pumping a well. For the purposes of evaluating the effects of a pollution source on the regional flow system, the pollution source can be treated as an injection well. The expression describing the boundary of the affected downgradient region (ignoring dispersivity) is as follows:

$$-(y/x) = \tan(2KbI/Q)y \qquad \text{(Eq. 2.1)}$$

where K = hydraulic conductivity, in liters per day per square meter

b = aquifer thickness, in meters

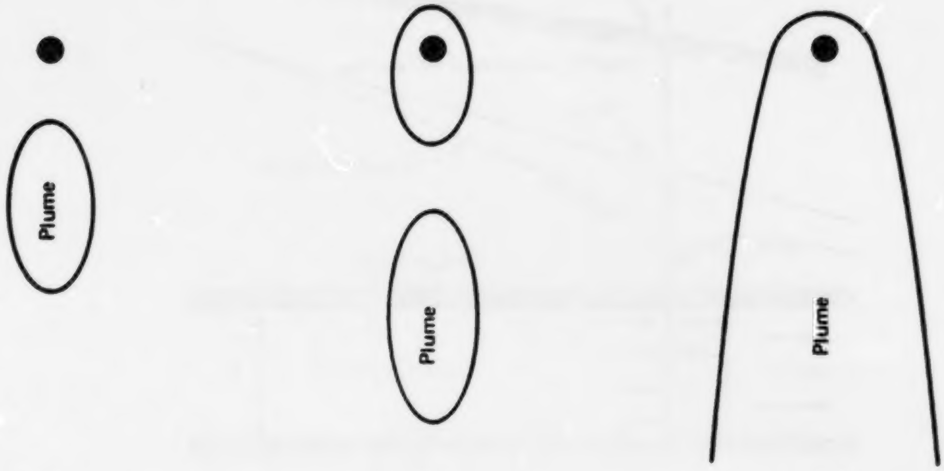
I = hydraulic gradient, in meters per meter

Q = leakage rate from the source, in liters per minute

The rectangular coordinates (x and y) are as shown in Figure 2.7 with the origin at the center of the source.

Based on the expected type of plume, a decision can be made concerning how often in the flow path samples are required for adequate definition of plume dynamics. This decision can then be translated into

TYPE OF PLUME GENERATED FROM (a) A SLUG SOURCE OR SPILL, (b) AN INTERMITTENT SOURCE, AND (c) A CONTINUOUS SOURCE


Plume
Plume
Plume

(a) (b) (c)

Figure 2.6

RESULTING CHANGE OF A CAPTURE AREA DUE TO REGIONAL FLOW (After ref. 42)

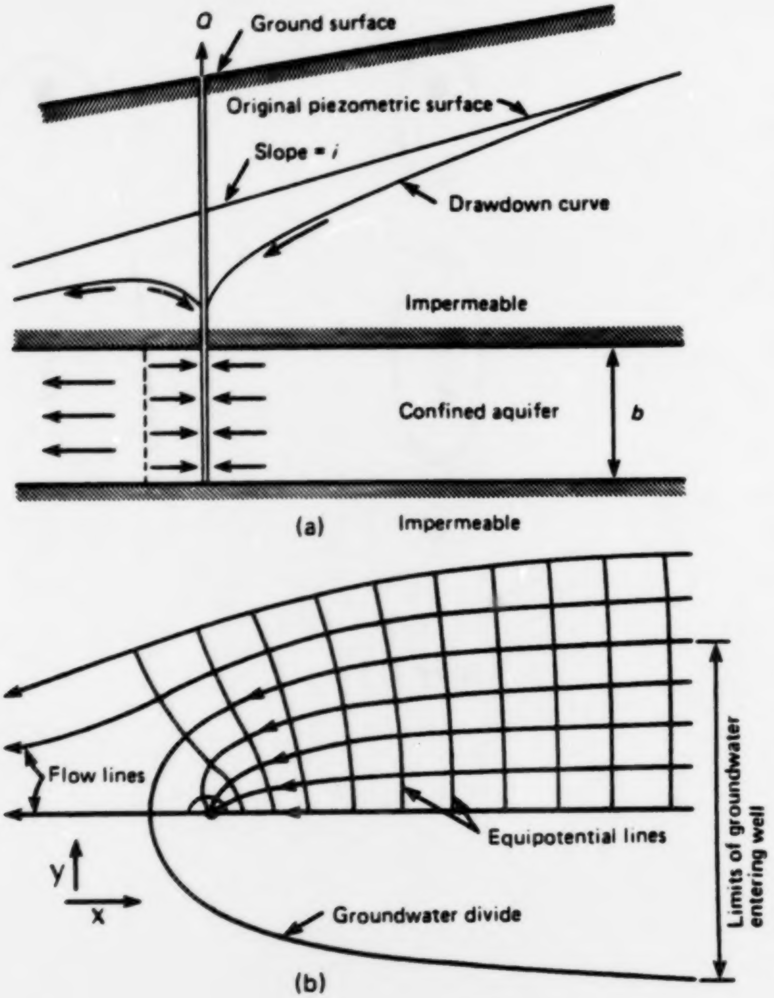

Q
Ground surface
Original piezometric surface
Slope = i
Drawdown curve
Impermeable
Confined aquifer
b
(a)
Impermeable
Flow lines
Equipotential lines
y
x
Groundwater divide
Limits of groundwater entering well
(b)

Figure 2.7

a sampling frequency using the hydrogeologic parameters measured at the site. The velocity of ground-water flow is described using Darcy's equation and the effective porosity of the materials being monitored:

$$v = KI/7.48N \qquad \text{(Eq. 2.2)}$$

where v = velocity of ground-water flow, in meters per day

K = hydraulic conductivity, in liters per day per square meter

I = hydraulic gradient, in meters per meter

N = effective porosity, in percent

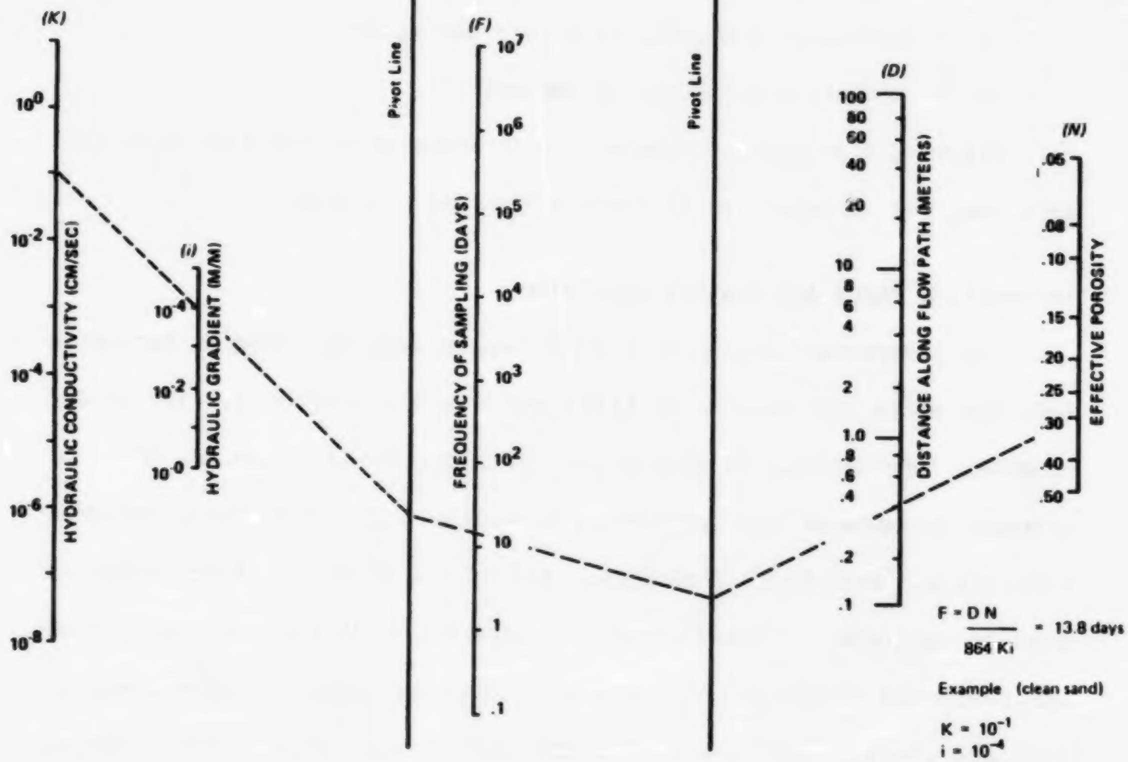
Figure 2.8 presents a nomograph for translating the hydraulic data into sampling frequencies at various flow path lengths.

INFORMATION NEEDS AND ANALYTE SELECTION

The information needs of a ground-water sampling program determine both the scope and details of field and laboratory efforts. The needed chemical information, in particular, will drive the selection of techniques, procedures and methodologies which will constitute integral sampling and analytical protocols. All of the steps in these protocols must be tailored to the analytes of interest by a well conceived plan for field and laboratory operations. Detailed data on source composition and the type or extent of contamination available to most initial investigations is usually limited. This is particularly true of ground-water investigations at waste management facilities. Regardless of the state of the information base, the planning effort must incorporate flexibility to meet a variety of contingencies.

It is often more cost-effective and reasonable to plan the effort for the maximum long-term return on the investment of fiscal and human

SAMPLING FREQUENCY NOMOGRAPH



$$F = \frac{D\,N}{864\,Ki} = 13.8 \text{ days}$$

Example (clean sand)

$K = 10^{-1}$
$i = 10^{-4}$
$N = 0.30$
$D = 0.4$ meters

Figure 2.8

resources. Therefore, the planning effort should anticipate difficulties and allow for refinement of the sampling and analytical protocols as new data becomes available.

The basis of a successful monitoring program is a robust, integral sampling protocol, coupled to proven analytical schemes. Both field and laboratory personnel should be involved in planning, once the minimum information needs of the program are identified. In this way, the potential impact of seemingly minor details of the program protocols can be judged more appropriately.

Parameter Selection

Parameter selection for chemical measurements is very important to the effective planning of sampling and analytical protocols. For exploratory efforts, it is useful to obtain slightly more chemical and hydrologic data than that required by the immediate information needs of the program. The added data can normally be put to good use as the site conditions become better defined. For example, in a situation where essentially no chemical data for a site exists, a complete mineral analysis should be included. The results provide an internal consistency check on major ionic constituents, field determinations (e.g. alkalinity) and the potential effects of unusually high levels of metals or nutrient anions (16,23). Reliable analytical methods for ionic constituents and routine field determinations (pH, Eh, temperature, conductance and alkalinity) are well referenced for ground-water samples by the USEPA (27,28,29) and various other groups (45,46). The results of the complete mineral analysis and field determinations define the major ion solution chemistry which is quite valuable to obtaining an overall picture of the subsurface system of interest. The major ion chemistry determines the inorganic background and potential for matrix effects in sampling and analysis. Chemical speciation of many specific inorganic constituents of interest (e.g. Fe, Cu, Pb) may be controlled by the inorganic solution chemistry. In turn, the speciation of the chemical constituents of interest effects subsurface transport behavior and sensitivity to either handling disturbances or recovery in analytical separations.

With a complete mineral analyses and a clear view of information needs, one can then select the additional chemical parameters of interest. These parameters may be characterized as general ground-water quality parameters, pollutant indicator parameters and specific chemical contaminants.

General Ground-Water Quality Parameters

Parameters which give a general overview of ground-water quality relate to total dissolved solids content (e.g. Na^+, Cl^-, $SO_4^=$) and traditional water treatment difficulties of ground water. Taste or odor removal needs associated with the presence of dissolved iron, manganese and total phenols vary substantially among ground-water supplies. Beyond The determination of ground-water quality parameters may also provide an indication of severely contaminated conditions. The choice of sample collection and handling methods should be given careful consideration. Degassing (e.g. loss of CO_2) and oxygenation (e.g. loss of Fe, trace metals) can markedly effect analytical results, even for water quality constituents at the ppm ($mg \cdot L^{-1}$) level (11). The sensitivity of the results for these water quality parameters to sampling procedures is a function of the major ion chemistry and chemical speciation. Therefore, complete mineral analyses should be included in most sampling programs, if only on a limited basis.

Pollution Indicator Parameters

Contaminant monitoring program requirements for parameter selection reflect the following objectives: to detect whether or not the operation of a facility results in the contamination of ground water, to determine whether concentrations of specific chemical constituents are within prescribed limits, and to measure the effectiveness of corrective actions. In general, contaminant monitoring program approaches are of two types.

The generic approach requires the determination of parameters indicative of gross disruption of the inorganic or organic chemistry of subsurface conditions [e.g. pH, solution conductivity (Ω^{-1}), total organic carbon (TOC) and total organic halogen (TOX)]. It is a low cost analytical alternative, generally applied in detective monitoring situations. The rationale is that these surrogate parameters will indicate the impact of waste releases to ground-water systems and suggest the identity of the major classes of the chemical constituents involved. The usefulness of pH and Ω^{-1} have been mentioned above in relation to their importance to total dissolved solids content and major ion chemistry of ground-water samples.

Prior to the detection of water quality changes and in the absence of a complete mineral analysis, the usefulness of the indicator parameter approach is limited. This is especially true for TOC and TOX determinations which are nonspecific and are limited in sensitivity.

Sample collection and handling precautions must be optimized to insure that the volatile and nonvolatile fractions of both TOC and TOX are recovered quantitatively (47). Otherwise, the significance of these generic parameters may be misrepresented and systematic errors in sampling or analysis will negate their utility as diagnostic tools. It should be pointed out that the use of TOC and TOX as pollution indicator parameters can enhance the interpretative power of observed data on specific contamination distributions at substantially lower cost. The trade off, of course, is that transformations of specific volatile or nonvolatile contaminants may go unobserved. The second contaminant monitoring approach focusses on a more specific set of chemical constituents.

Specific Chemical Constituents

Several alternative approaches to generic contaminant monitoring program emphasize the sampling and determination of specific mobile or persistent chemical constituents. The selection of parameters may be limited to those identified by law (e.g. Interim Primary Drinking Water Standards or Resource Conservation and Recovery Act--Appendix VIII parameters, etc.) or may be based on the actual composition of a regulated facility's waste streams.

The use of a specific list of chemical constituents should be approached cautiously. The determination of a legally mandated suite of parameters tends to focus primarily on specific classes of compounds in wide usage as starting materials for manufacturing or commercial product formulations. This type of program has definite advantages, particularly in situations where the spill or release of a product occurs (48).

However, detailed investigations of organic compound distributions in environments contaminated by organic mixtures disclose that by-products or substituted congeners of "priority-pollutants" may be the major mobile and persistent constituents, while those parameters mandated by compliance programs may be present only as minor trace components (49).

In situations where the original waste components or contaminant mixtures are known, it is preferable to consider the relative mobility and persistence of the known components, as well as potential transformation products. This mode of parameter selection demands a reasonable understanding of the situation under investigation. Most of the standardized procedures for sample collection, handling and analysis which function well in the initial phases of an investigation may have to be modified to insure control of errors when applied to specific contaminants (18,50,51). Once the likely suite of target chemical constituents has been developed, the sampling and analytical protocols should be thoroughly reviewed and modified appropriately.

It is important to keep in mind that sampling errors will be carried over into the analytical operations which follow. Generic sampling protocols recommended for use in ground-water investigations (52) should be proven to be compatible with the analytical procedures by careful consideration of accuracy, precision, sensitivity and completeness performance guidelines (26).

In order to maximize the cost-effectiveness and flexibility of the initial planning of a ground-water sampling program, it is useful to anticipate that the degree of analytical detail required will increase as the investigation proceeds. Therefore, it is wise to prepare the sampling protocol for the most troublesome chemical parameters which may be of interest and maintain close control over the sampling operations. Volatile organic compounds (e.g., benzene and trichloroethylene) which are soluble and frequent early indicators of more persistent contaminants are a good candidate group of chemical constituents on which the sampling protocol should be based. The principal errors introduced by the sample collection mechanism, materials' exposures and sample handling are due to degassing or volatilization and sorption or leaching effects. These errors are common to those involved in accurately determining major ion chemistry, TOC, TOX, trace inorganic and nonvolatile organic constituents to varying degrees, depending on the speciation and analytical sensitivity for the chemical contaminants of interest. In general, sample collection errors are systematic and directly affect the accuracy of all subsequent analytical results.

An inappropriate sampling mechanism (e.g. air lift mechanisms for volatile or gas sensitive parameters) can yield consistently inaccurate and useless results. The literature provides valuable guidance in the choice of appropriate sampling mechanisms and materials once the parameters of interest are identified with an emphasis on the more challenging problems posed by organic compounds (52,53). It is clear that sampling mechanisms which minimize gas exchange or materials' effects and permit well head determinations of pH, Eh, Ω^{-1} and temperature are those of choice for most detailed sampling programs. Sampling protocols are an active area of research, but one should keep in mind that it will cost less over the long-term if the investigation is planned correctly to meet information needs. High quality data merit the time and expense of detailed interpretation. Invalid or biased data, on the other hand, are expensive to evaluate and ultimately damage the credibility of the program.

Minimal Analytical Detail for Ground-Water Monitoring Programs

The minimum data set, sufficient to the information needs of the monitoring program, is defined by both geochemical and hydrologic considerations. Once the set of routine data elements necessary to define the situation at hand have been established, sampling frequency and completeness requirements will dictate the dimensions of the data set. For optimum data recovery and facile data interpretation, it is important to define the size of the data set and allow for expansion of the elements of interest. Computer assisted sample tracking procedures incorporated into the overall data management system (including analytical data handling) can facilitate data validation and trend analysis.

The following recommended data sets have been developed to coincide with detective, assessment and remedial action evaluation program goals. They provide a degree of analytical detail which can be checked for internal consistency. This is important to assure that the highest quality data are produced which are commensurate with the manpower and fiscal investments that high quality data collection demands.

Detection Monitoring Data Set

The minimal data set for a monitoring program designed for future detection of contamination should provide the base level of information on hydrologic and chemical conditions at a site. The parameters identified below will permit mass and charge balance checks on the consistency of the data and will provide valuable information on ground-water chemistry. In this manner, the ability to identify "missing" charged constituents, which may be contamination related, can be established.

Chemical Parameters

pH, Ω^{-1}, TOC, TOX, Alkalinity, Total Dissolved Solids

Eh, Cl^-, NO_3^-, $SO_4^=$, $PO_4^{\equiv}$, SiO_2

Na^+, K^+, Ca^{++}, Mg^{++}, NH_4^+, Fe, Mn

Hydrologic Parameters

Water Level, Hydraulic Conductivity

This level of detail provides the basis for solution chemistry composition calculations which are important for predictions of contaminant speciation, mobility and persistence.

Assessment Monitoring Data Set

The minimal data set for a monitoring program designed to assess the type and extent of contamination incorporates the level of detail noted in detective monitoring situations and indentifies potential contaminants of concern. The actual suite of potential contaminants may be stipulated by regulation in some instances.

Chemical Parameters

pH, Ω^{-1}, TOC, TOX, Alkalinity, Total Dissolved Solids

Eh, Cl^-, NO_3^-, $SO_4^=$, $PO_4^{\equiv}$, SiO_2, B

Na^+, K^+, Ca^{++}, Mg^{++}, NH_4^+, Fe, Mn

Fe(II), Zn, Cd, Cu, Pb, Cr, Ni

Ag, Hg, As, Sb, Se, Be

Hydrologic Parameters

Water Level, Hydraulic Conductivity

The realm of potential organic contaminants in ground-water systems must be delimited based on the nature of the likely contaminant source. The priority pollutant analytical scheme or selected categories of RCRA Appendix VIII parameters should be a good starting point when other data are unavailable.

WELL PLACEMENT AND CONSTRUCTION

The placement and construction of monitoring wells are among the most difficult decisions involved in developing an effective monitoring program. The preliminary locations and depths of monitoring wells should be selected based on the best available pre-drilling data. Then as the actual installation of these wells progresses, new geologic and hydrologic data should be incorporated into the overall monitoring plan to insure that the finished wells will perform the tasks for which they are designed. In most instances, it is probably advisable to select a minimum array of monitoring wells for the collection of geologic and hydrologic data. Then additional wells can be designed and constructed to more effectively meet the goals of the monitoring program.

The positioning of a monitoring point in a contaminant flow path must be determined on the basis of hydrologic data. Therefore, the contaminant flow path must be clearly defined in three dimensions. Special emphasis must be placed on the collection of accurate water level data as well drilling and construction progress. For example, the level at which sand heaves up into the borehole is often related to the depth at which the vertical movement of ground water is upward as opposed to the normally assumed downward migration. Accurate measurements of stabilized water levels from an established reference elevation is essential to understanding the flow paths of ground water and dissolved constituents.

The construction of monitoring wells should be accomplished in a manner that minimizes the disturbance of the materials in which the well is constructed (3). If the monitoring program calls for determinations of organic compounds, care should be taken to steam clean the drill rig and all other equipment and well components prior to mobilization to the site. Repeated cleaning of drilling equipment and well-construction materials at the site also is necessary. The drill rig should be checked for hydraulic fluid and oil leaks prior to the initiation of drilling. These preliminary precautions are essential to insure that artefacts of the drilling process are not detected later in the program and considered to be the result of actual conditions at the monitored facility.

The selection of the type of drilling equipment should depend on the type of geology present, the expected depths of the wells, and the availability of equipment in the location of interest. However, the availability and relative costs of different types of drilling equipment should not be used as the primary selection criteria. The use of specialized drilling techniques may have real advantages for even the most preliminary site investigations (50).

Drilling and Well Completion Methods

The selection of drilling and well completion methods for monitoring well construction has been approached traditionally from considerations of the type of geologic materials to be penetrated, the anticipated depth of drilling, and the availability of construction equipment and materials. Little attention has been given to the potential adverse chemical effects of the drilling and well construction procedures on the samples produced from the monitoring well. This guide discusses several drilling methods in terms of the suitability of their application for monitoring well construction. Detailed discussions of drilling procedures and rigs are presented in other references (3,54).

The selection of an appropriate drilling method for constructing monitoring wells should be based on minimizing both the disturbance of the geologic materials penetrated and the introduction of air, fluids, and muds. The use of organic drilling muds or additives should be avoided. The introduction of any foreign material has the potential for interfering with the chemical quality of water obtained from the monitoring wells. Based on these factors and the physical limits of the various drilling methods and rigs, the following evaluations have been made of the more commonly used types.

A summary of recommended applications for various drilling techniques is presented in Table 2.1.

Hollow-Stem Continuous-Flight Auger

The hollow-stem continuous-flight auger rig is among the most desirable drill rigs for the construction of monitoring wells. The rigs are generally mobile, fast, and inexpensive to operate in unconsolidated materials. No drilling fluids are used and disturbance to the geologic materials penetrated is minimal. However, augers cannot be used in consolidated rock and most rigs are limited to drilling to approximately

Table 2.1. Recommended Drilling Techniques for Various Types of Geologic Settings

Geologic Environment	Recommended Drilling Technique
Glaciated or unconsolidated materials less than 150 feet deep	(1) Hollow-stem continuous-flight auger (2) Solid-stem continuous-flight auger (3) Cable tool
Glaciated or unconsolidated materials greater than 150 feet deep	(1) Cable tool
Consolidated rock formations less than 500 feet deep (minimal or no creviced formations)	(1) Cable tool (2) Air rotary with casing hammer (3) Reverse circulation rotary
Consolidated rock formations less than 500 feet deep (highly creviced formations)	(1) Cable tool (2) Air rotary with casing hammer
Consolidated rock formations more than 500 feet deep (minimal or no creviced formations)	(1) Air rotary with casing hammer
Consolidated rock formations than 500 feet deep (highly creviced formations)	(1) Air rotary with casing hammer

45.5 m (150 feet) (3). In formations where the bore hole will not stand open, the well is constructed inside the hollow-stem augers prior to their removal from the ground. This limits the diameter of the well that can be constructed with this type of drill rig to about 10.16 cm(4 inches). 15.24 cm (6-inch inside diameter augers are available for this purpose. The use of hollow-stem auger drilling in heaving sand environments also presents some difficulties for the drilling crew. However, with care and the use of proper drilling procedures, this difficulty can be overcome.

Solid-Stem Continuous-Flight Auger

The use of solid-stem continuous-flight auger drilling techniques for monitoring well construction is limited to relatively fine grained unconsolidated materials that will maintain an open bore hole. The method is similar to the hollow-stem continuous augers except that the augers must be removed from the ground to allow the insertion of the well casing and screen. This method is also limited to a depth of about 45.5 m (150 ft) and does not lend itself to collection of soil or formation samples. This type of drilling method is a poor second choice to the more desirable hollow-stem auger methods.

Cable Tool

The cable tool type of rig is relatively slow but still offers many advantages that make it the second choice for monitoring well construction in unconsolidated formations and the method of choice for relatively shallow consolidated formations. The method allows for the collection of excellent formation samples and detection of even relatively fine grained permeable zones. The installation of a steel casing as drilling progresses also provides an excellent temporary host for the construction of a monitoring well once the desired depth is reached.

As stated earlier, the method is slow and small amounts of water must be added to the hole as drilling progresses until the water table is encountered. However, the quantity of water added to the hole and into the formation to be sampled is minimal. A drive pipe diameter of 10.16 cm (4 inches) may be too small for the easy construction of a 5.08 cm (2-inch) diameter well. It is recommended that a minimum 15.24 cm (6-inch) diameter drive pipe be used to facilitate the placement of the well casing, screen, and gravel pack, and a minimum 152.4-cm (5-foot) long bentonite seal prior to beginning the removal of the drive pipe. The placement of a bentonite seal in the drive pipe prior to pulling will assist in holding the gravel pack, well casing, and screen in place. The seal will also isolate the gravel pack and screen from the cement seals above. The drive pipe is pulled in small increments to permit the bentonite seal to flow outward and fill the annular space vacated by the drive pipe. The drive pipe also is pulled in small increments as cement grout material is added to ensure that a satisfactory seal is obtained.

Air Rotary

Rotary drilling methods operate on the principle of circulating either a fluid or air to remove the drill cuttings and maintain an open hole as drilling progresses. The different types of rotary drilling are named according to the type of fluid and the direction of fluid flow. Air rotary drilling forces air down the drill pipe and back up the bore hole to remove the drill cuttings. The use of air rotary drilling techniques is best suited for use in hard rock formations. In soft unconsolidated formations a casing is driven to keep the formations from caving. Similarly, in highly creviced formations it is often difficult to maintain air circulation. Air rotary drilling appears to have potential for constructing monitoring wells without adversely affecting the quality of water from monitoring wells in hard rock formations with minimum unconsolidated overburden. The successful construction of monitoring wells using this drilling techniques is dependent on the ability to maintain an open bore hole after the air circulation ceases. If the wells are intended to monitor for organic constituents, the air from the compressor on the rig must be filtered to insure that oil from the compressor is not introduced into the geologic system to be monitored. The addition of foam to the circulating air is often employed to increase the effectiveness of air drilling techniques. Most of the foam additives contain organic materials which may interfere with both organic and inorganic constituents in samples collected from the constructed monitoring wells. The use of air rotary drilling techniques should not be used in highly polluted or hazardous environments. Contaminated solids and water are blown out of the hole which are difficult to contain. Protection of the drill crew and observers is correspondingly very difficult.

Air Rotary With Casing Hammer

Air rotary drilling with casing driving capability increases the utility of this type of drilling method. The problems associated with drilling in soft unconsolidated and highly creviced formations are minimized. The utility of constructing monitoring wells in the casing prior to pulling it also makes this type of drilling technique more appealing. However, the same concerns about the oil in the circulating air and the addition of foam additives must be considered. Grouting and casing pulling procedures similar to those described for cable tool drilling methods should be employed.

Reverse Circulation Rotary

Reverse circulation rotary drilling has limited application for the construction of monitoring wells. Large quantities of water are circulated down the bore hole and pumped back to the surface thru the drill stem. The hydrostatic pressure of the water in the bore hole is used to maintain an open bore hole. If permeable formations are encountered, large quantities of water will infiltrate into those formations altering *in situ* water quality. Similarly, water bearing units with differing hydrostatic heads will have the opportunity for free interchange of waters altering the quality of water in the unit of lower hydrostatic head. Because of the large quantities of water normally required for this type of drilling and the high potential for water to enter the formations to be sampled, this type of drilling is not recommended.

Mud Rotary

Mud rotary drilling operates in the same fashion as the air rotary drilling technique except water and drilling mud are circulated down the drill pipe and back up the bore hole to remove the drill cuttings. The bore hole is held open by the hydrostatic pressure of the circulating mud and a mud cake that develops on the bore hole wall during the drilling process. The viscosity of the drilling mud is controlled to minimize the infiltration of the drilling fluid into porous formations penetrated by the drilling equipment.

The construction of monitoring wells using mud rotary drilling techniques is very difficult. The well must be constructed in the bore hole which is still filled with drilling mud. This makes it difficult to determine where gravel pack materials terminate and the well seal begins. After monitoring wells are constructed, they must be developed to produce visually clear water which will facilitate field filtration. Breaking down the mud cake and removal of all mud introduced by this drilling technique is extremely difficult when small diameter monitoring wells are being constructed. Experience has shown that drilling muds not effectively removed from the well bore opposite the screen and gravel pack will interfere with the chemical and biological quality of samples from those wells (55,56,57). Many clay or synthetic drilling muds contain organic matter (e.g., polymers, polyacrylamide or starches) which can also greatly effect the organic content of water obtained from mud rotary drilled wells (23,47). For these reasons, the use of mud rotary drilling methods is not recommended, particularly for investigation of organic contaminant situations.

Bucket Auger

Bucket auger drilling rigs are usually employed for the construction of shallow large diameter wells or caissons. Their use is limited to fine grained formations that are capable of supporting an open bore hole. The large diameter created by this type of drilling technique is not usually warranted. The use of hollow-stem continuous-flight auger techniques can be more effectively employed in appropriate geologic environments.

Jetting

Jetting of monitoring wells is not a common practice in most of the United States. Little or no information is obtained on the materials thru which the well is jetted. As with the reverse rotary drilling technique, water used in the jetting process also enters the formation to be monitored and alters the in situ water quality. This type of drilling technique is not recommended for monitoring well construction.

Driving

Driving of well points and casing may be acceptable in certain hydrogeologic environments. As with jetting, little or no information is obtained on the materials through which the well is driven. This type of well construction should be limited to relatively shallow (less than 15.17 m (50 feet)) homogenous sand and gravel formations. Due to the nature of this geologic environment, no well seals are normally required.

Monitoring Well Design

The effective design of monitoring wells requires careful consideration of the hydrogeology and subsurface geochemistry at a site. The information obtained from preliminary borings or well drilling can be most useful in making logical decisions on the drilling, construction and development methods which are appropriate for the program's goals. The design of a monitoring well should not be based on the most readily available types of drilling equipment or that used by the favorite driller in the area where the project is located. Cost considerations alone should be secondary to the retrieval of valid data which will meet the goals of the program. Apparent cost savings realized by expedient well construction may have a serious impact on the quality of the hydrologic and chemical data produced from the monitoring effort. The well design goal should be to construct wells that will produce depth and location specific hydrologic and chemical data. Precautions must be taken to insure that well completion and development procedures minimize the disturbance to the geologic environment and the water samples.

Wells constructed for the production of large quantities of water normally are not satisfactory for use as monitoring wells in detective or assessment type monitoring programs. These wells are constructed with long sections of well screen or open bore holes designed to produce water from large vertical and horizontal segments of the aquifer materials tapped. The resulting chemical quality of water pumped from the wells represents an integrated chemical quality from all sections of the aquifer contributing water to the well. Without knowledge of the vertical and horizontal contributions of water to the well, these chemical data have little value aside from indicating the quality of water produced by that well. A potentially large amount of dilution of any relatively small plumes (relative to the size of the pumping cone) intersected by the pumping cone of the well could effectively mask the presence of the plume. Similarly, the hydrologic data obtained from these types of wells represents an integrated water level for the vertical segment of the aquifer open to the well. The hydraulic conductivity data represent integrated values for the segments of the aquifer influenced during the course of the pumping test.

Depth of the Well

The depth of a monitoring well should be determined based on the geology and hydrology of the site and the goals of the monitoring program. In most monitoring programs the goal is to monitor the potential effects of near surface activity. Therefore, it is essential to document and monitor the downward migration of potential pollutants that may be leaking from the facility. As percolating water and their solutes move into the saturated zone, local and region flow systems are encountered that will impart a horizontal component to the migration of the pollutants.

To properly define the movement of pollutants, vertically and horizontally, it is essential to collect depth discrete water level data. The uppermost relatively permeable zone will provide part of the data needed to determine the vertical direction of ground-water movement. The shallowest monitoring wells in the monitoring system should be finished in these materials. Water levels from these wells, if finished in the same geologic materials, will provide information on the horizontal directions of shallow ground-water flow. In unconfined aquifer systems this will represent the "water table." In confined aquifer systems it represents the piezometric surface of the shallowest permeable zone.

Additional wells at the same locations but at greater depths are needed to complete the data set needed to determine the vertical direction of ground-water movement. These wells should be finished in the next deepest relatively permeable zone in a geologic setting where interbedded permeable and nonpermeable zones are present. In geologic settings where the materials are relatively permeable and uniform with depth, the screens of adjacent wells should be staggered at an interval equal to one to three times the selected screen depending on the vertical detail necessary to define contaminant distributions. This vertically-nested well depth approach should be continued at each well location until water level data indicates that the potential for deeper migration of surface derived pollutants is minimal.

The required number of vertically nested wells and their depths also will be a function of the relative horizontal to vertical permeabilities of the formations beneath the site and the hydrologic setting in which they are located. The optimum approach is to ensure that the vertical locations of the well screens are at the most likely depth to intersect pollutants from the facility being monitored. An example is presented below to illustrate the application of this type of monitoring well design approach.

Example 2.1. Selecting depths for vertically nested wells in an alluvial river valley setting--

Site background:

> The site to be monitored lies on the banks of a major river. Regional information indicates that the unconsolidated materials are sand and gravel from the surface to the underlying bedrock, about 120 feet. Regional water levels vary from about 15 to 25 feet below land surface. The activity to be monitored is a small metal plating facility that

uses a lagoon for disposal of its wastes. The relative specific gravity of the wastes is similar to that of the native ground water. No hydrocarbons are associated with the wastes.

Preliminary well construction:

Locations for vertically nested wells were selected at one upgradient and three downgradient locations. Two wells, one about five feet below the seasonally low water table elevation and one approximately ten feet deeper, were constructed at each location. The wells were all equipped with two-foot long screens. The wells were developed, elevations of the casing tops (water level measuring reference point) were surveyed to the nearest 0.01 feet, and water levels were measured to the nearest 0.01 feet.

Preliminary water level analysis:

The following list presents the construction, elevation, and water level data obtained from this preliminary and a subsequent second drilling effort.

Well no.	Depth below land surface	Land surface elevation	Elevation midpoint screen	Measuring point elevation	Water level below MP	Water level elevation
BG-1	32.0	349.27	318.27	352.00	22.00	330.00
BG-2	42.0	349.27	308.27	351.85	22.65	329.20
DG1-1	26.0	344.11	319.11	346.69	23.29	323.40
DG1-2	36.0	344.11	309.11	346.53	23.73	322.80
DG2-1	27.0	343.42	316.42	345.97	23.89	322.08
DG2-2	37.0	343.42	306.42	345.78	24.18	321.60
DG3-1	26.0	339.73	313.73	342.71	22.61	320.10
DG3-2	36.0	339.73	303.73	342.59	22.61	319.98
Second drilling effort:						
DG1-3	46.0	344.11	299.11	346.37	23.62	322.75
DG2-3	47.0	343.42	296.42	345.53	24.11	321.42
DG2-4	57.0	343.42	286.42	345.29	24.19	321.10
DG3-3	46.0	339.73	293.73	342.31	22.26	320.05
DG3-4	56.0	339.73	283.73	342.17	21.97	320.20

At each of the vertically nested well pairs, the direction of ground-water movement is downward. Plotting the total hydraulic head (water level elevations) at the midpoint of the well screens and constructing flow path lines from the proposed lagoon facility suggests that deeper wells are required at DG1, DG2, and DG3.

Second drilling effort and analysis:

> One additional well was constructed at DG1 and two additional wells were constructed at DG2 and DG3. Data from those wells are included in the above table. Plotting the total hydraulic heads at the midpoints of the well screens and constructing flow paths suggests that these wells should be adequate for monitoring potential leakage from the lagoon. Figure 2.9 illustrates the analyses of data and plotting of vertical and horizontal flow paths. From this preliminary data, the appropriate wells for sampling and chemical analysis can be selected.
>
> As a final word of caution, this planning and construction effort was accomplished during a period of low water levels; data from periods of high water levels should be examined to determine if the same well configuration is adequate. Similarly, these analyses were conducted prior to the influences of leakage from the lagoon. The same type of water level analyses should be performed periodically to insure that the monitoring program remains effective in meeting the intended goals.

In addition to the general guidelines noted above, wells intended for use in monitoring hydrocarbon pollutants that are less dense than water and likely to float on the water table surface should be constructed so the well screen is always open to the water table. If the water table is known to fluctuate several feet over the course of the year, the screen will have to be long enough to accommodate those fluctuations.

The design of monitoring wells for sampling sites contaminated with immiscible hydrocarbons or hydrocarbon products more dense than water also warrants special consideration. A well screened throughout the entire thickness of the aquifer potentially affected appears to offer the best potential for adequately addressing this type of monitoring problem (58). Wells constructed in this manner and properly sampled to

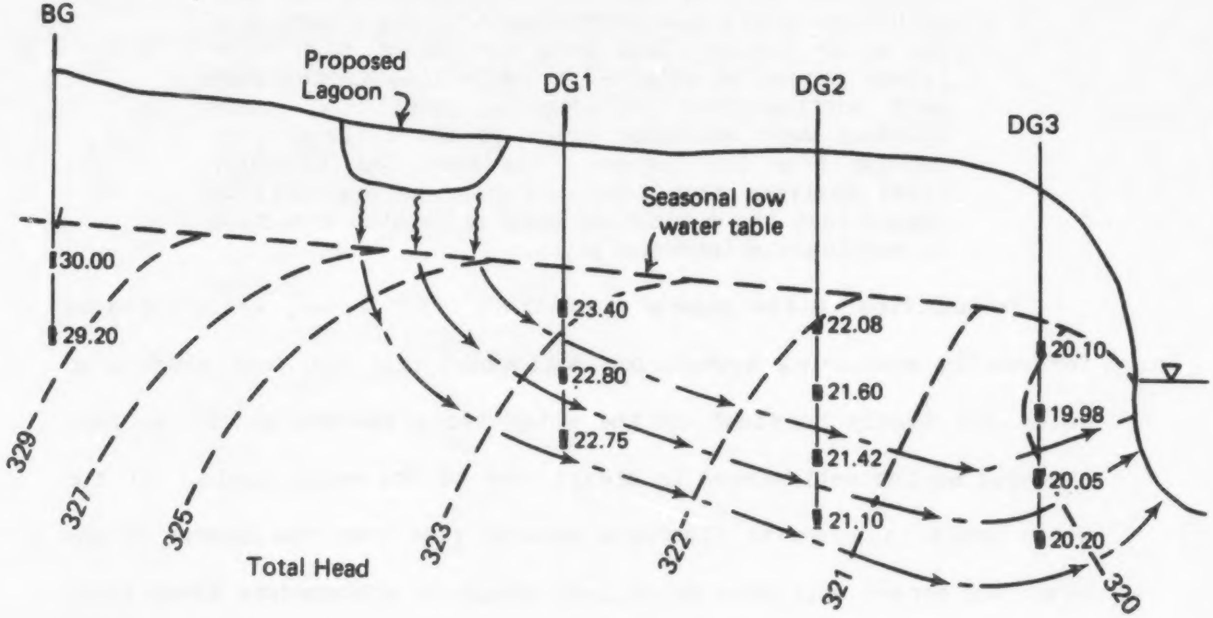

BG
Proposed Lagoon
DG1
DG2
DG3
Seasonal low water table
30.00
29.20
23.40
22.80
22.75
22.08
21.60
21.42
21.10
20.10
19.98
20.05
20.20
329
321
325
323
322
321
320
Total Head

Figure 2.9. Well placement and flow paths at low water levels

minimize the vertical migration of non-aqueous phases within the well should provide reasonable indications of the vertical distributions of hydrocarbons in the aquifer system.

Diameter of Monitoring Wells

The diameter of a monitoring well casing should be held to the minimum practical size which will meet both the strength requirements for the anticipated well depth and the size of the sampling pump required to deliver water samples to the surface. Studies by Gibb (11) have documented that the water held in storage in the well casing undergoes chemical change while in the well casing. When pumping begins for sample collection, some of this chemically altered water will be brought to the surface along with water from the formation being sampled. The relative quantity is related to the hydraulic conductivity of the formation being sampled, the rate at which the well is pumped and the size (diameter) of the well casing. The amount of water removed from the well casing is a function of the formation hydraulic properties and the pumping rate. Therefore, as the diameter of the well increases, larger portions of altered, unrepresentative, water samples are delivered to the surface to create the same amount of drawdown. Based on the availability of ground-water sampling pumps capable of lifting water from depths as great as 15.17 to 227.50 m (500 to 750 feet), 5.08-cm (2-inch) diameter wells should be used in all situations except where depth requirements call for added material strength. Table 2.2 presents general depth recommendations for various sizes of PVC, stainless steel, and Teflon(R) well casings.

Table 2.2. Well Casing Material Specifications Depth Recommendations

	PVC		Stainless steel		Teflon
	Schedule 40	Schedule 80	Schedule 40	Type 304	Schedule 40
Nominal casing diameter	2"	2"	2"	2"	2"
Wall thickness	0.154"	0.218"	0.065"	0.065"	0.080"
Weight lbs/ft	0.716	0.932	1.732	1.732	0.9
Type of thread	square	square	fine	square	square
Maximum recommended hang length* (ft)	3,100	3,300	11,500	Not available	320

* Length refers to total of single material. Depth range of Teflon(R) can be extended by casing only the saturated zone with this material using another material above. The hang lengths were calculated on the baiss of the shear strength of the threads and the weight of the suspended casing.

Size of Screen

The screen in a monitoring well should be long enough to permit entry of water from the vertical zone to be monitored. In most geologic settings a 60.96-cm (2-foot) long screen is adequate. The length of the screen should be held to a minimum so that water level data obtained from the well will represent relatively depth discrete information. In wells where the length of the screen is long [152.40 cm (5 feet) or more] the resulting water level is an integrated value representing an average water level of the materials opposite the screen.

The slot size of the screen also should be selected to retain the formation materials yet permit free entry of water into the well. Since most monitoring wells are not pumped at high flow rates the available open area of the screen is not usually an issue as in production well screen design. In very fine grained deposits a gravel pack material is often placed between the screen and the formation to be monitored. The grain size of the pack material should be three to five times the average grain size of the formation materials. The screen slot size should be selected to retain 90% of the gravel pack materials. When Teflon(R) casing and screen are used in deep formations, it is recommended that a slightly larger screen slot size be used since the Teflon(R) will tend to compress and reduce the effective slot size. The gravel pack materials should be thoroughly cleaned and composed principally of quartz sand. Materials containing fine grained clay or silt sized particles should be avoided. The chemical nature of the pack material should be as inert as possible. Silica sand or glass beads are recommended.

For wells where no gravel pack is used, the screen slot size should be selected to retain 60 to 70% of the materials opposite the screen. The finer portions of the aquifer materials are removed from the formation during well development and a natural gravel annulus is created around the well screen.

Grouts and Seals

The selection of grouts and seals for monitoring wells is an essential consideration to obtain water samples that are representative of in-situ conditions. First, the seal must be adequate to prohibit the entry of surface water down along the well casing. Similarly, a good seal must be maintained along the entire length of the well casing to ensure that water from overlying formations does not migrate downward. Effective seals are obtained by using expanding materials that will not shrink away from the well casing after setting. Expanding neat cement and bentonite clay or a mixture of neat cement and bentonite clay are among the most effective materials for this purpose.

The selected seal also must not interfere with the water chemistry results. Bentonite clay has appreciable ion exchange capacity which may interfere with the chemistry on collected samples when the grout seal is in close proximity to the screen or well intake. Similarly, expanding cement which does not harden properly may affect the pH of water from monitoring wells when in close proximity to the well screen or intake.

To minimize these potential interferences, a 30.48-cm (1-foot) layer of fine Ottawa or silica sand should be place above the selected gravel pack. Then, if possible, 30.48 to 60.96 cm (1 to 2 feet) of bentonite pellets should be placed in the hole to prohibit the downward migration of bentonite slurry or neat cement. The upper 152.40 to 304.80 cm (5 to 10 feet) of the well casing should be sealed with expanding neat cement to provide for security and an adequate surface well seal. The exact depth of the upper seal should be slightly deeper than the probable deepest frost penetration. This will protect the well from frost heaving.

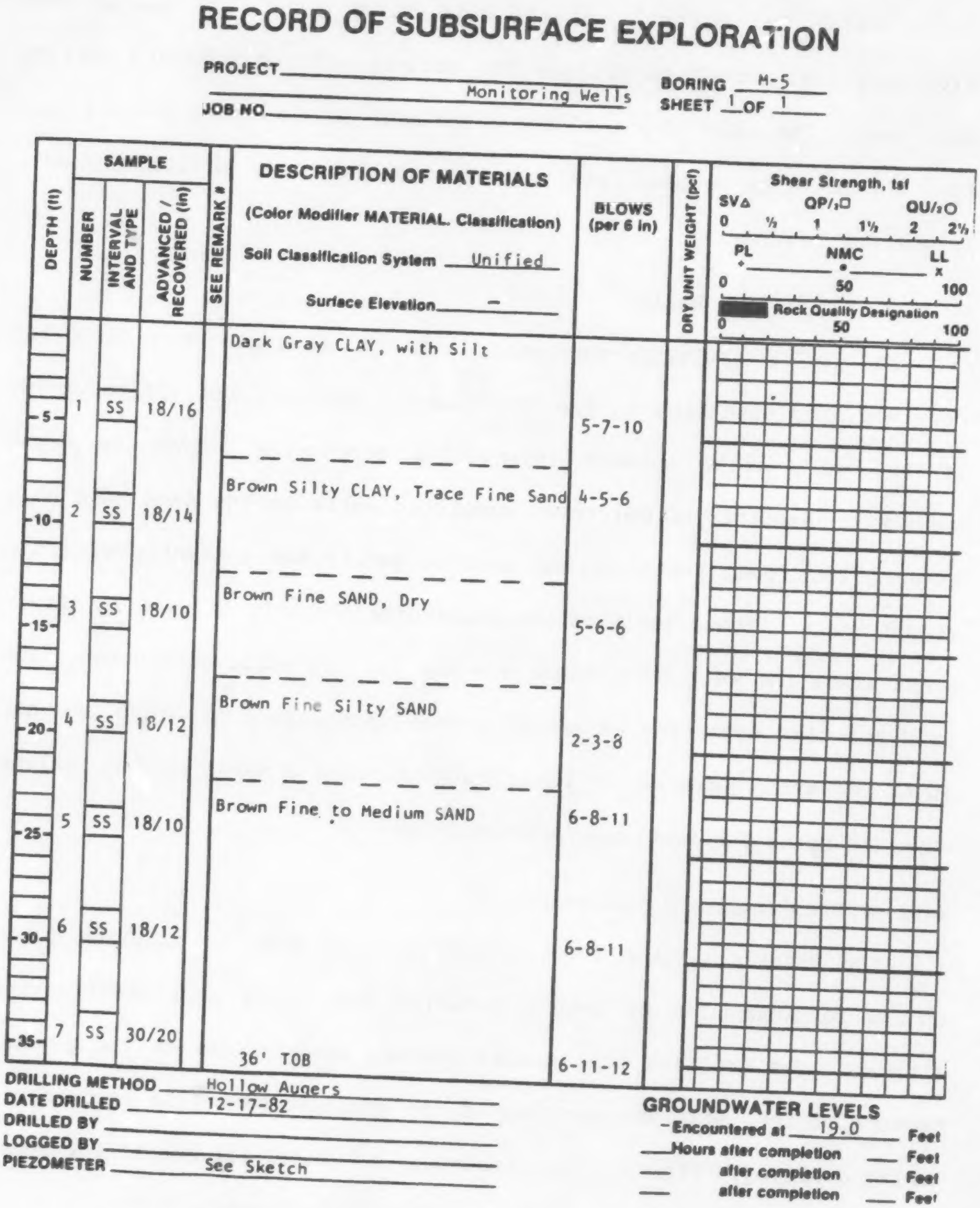
Multiple-Completion Wells

The use of multiple-completed wells in a single bore hole has received much attention in the literature. However, the effectiveness of the well seals between intervening monitoring points is often suspect. Advocates of multiple completed wells in the same bore hole suggest that pump tests can be used to verify the integrity of individual seals. These verification procedures can only be used in situations where the well completions are not in hydraulic connection. The care and time necessary to properly seal these types of wells are not justified when compared to the straightforward procedures for sealing separate holes for vertically nested wells.

Well or Sampling Point Documentation

The details of the construction of each well or sampling point should be documented by both a drilling log and a well construction diagram. The drilling log should contain descriptions of the general texture, color, size and hardness of the geologic materials encountered during drilling. Figure 2.10 illustrates a typical log containing these types of information in an easily understandable format.

Geophysical (earth resistivity or seismic) data should be mapped and correlated with data from the soil borings. Neutron or beta logging


Shear Strength, tsf
SV△
QP/₂□
QU/₂○
0
½
1
1½
2
2½
PL
NMC
LL
0
50
100
Rock Quality Designation
0
50
100

RECORD OF SUBSURFACE EXPLORATION

PROJECT Monitoring Wells
JOB NO.
BORING M-5
SHEET 1 OF 1

Soil Classification System Unified
Surface Elevation –

DEPTH (ft)	SAMPLE NUMBER	INTERVAL AND TYPE	ADVANCED / RECOVERED (in)	SEE REMARK #	DESCRIPTION OF MATERIALS (Color Modifier MATERIAL. Classification)	BLOWS (per 6 in)	DRY UNIT WEIGHT (pcf)
5	1	SS	18/16		Dark Gray CLAY, with Silt	5-7-10	
10	2	SS	18/14		Brown Silty CLAY, Trace Fine Sand	4-5-6	
15	3	SS	18/10		Brown Fine SAND, Dry	5-6-6	
20	4	SS	18/12		Brown Fine Silty SAND	2-3-8	
25	5	SS	18/10		Brown Fine to Medium SAND	6-8-11	
30	6	SS	18/12			6-8-11	
35	7	SS	30/20		36' TOB	6-11-12	

DRILLING METHOD Hollow Augers
DATE DRILLED 12-17-82
DRILLED BY
LOGGED BY
PIEZOMETER See Sketch

GROUNDWATER LEVELS
– Encountered at 19.0 Feet
__ Hours after completion __ Feet
__ after completion __ Feet
__ after completion __ Feet

Figure 2.10. Drilling log sheet

results may also be included on the logs of the bore holes investigated. Natural gamma ray, gamma-gamma density (Cesium-137 source), and electromagnetic induction logs can be run inside plastic casings as small as 5.08 cm (2 inches) in diameter and in some cases may be adequate and more cost effective than collection of core samples for describing geologic conditions. Use of these techniques should be compared or truthed with a minimal number of core samples for visual and laboratory examination. In all cases, the dates of all activities should be recorded to permit the reconstruction of the development of site understanding.

Data summaries in the form of geologic cross-sections are often very useful in developing a visual presentation of the subsurface conditions. However, caution must be exercised in interpolating between data points (soil borings). In very homogeneous geologic environments, extrapolations of data for tens to hundreds of feet may be acceptable. In more heterogeneous environments, extrapolation of data should not exceed a few tens of feet. To assess the relative homogeneity of the geologic environment, site specific data should be evaluated with respect to regional geologic information. No site description should be considered complete without an indication of the geologic variability of site conditions.

Once the bore hole is completed and well construction is underway, the data necessary for documenting well completion should be collected. The data items shown in Table 2.3 should be used to prepare a well construction diagram.

This information on well construction can be summarized on a one-page diagram similar to that shown in Figure 2.11. Geologic and preliminary water level data also should be included for completeness. The

Table 2.3. Data Needed for a Monitoring Well Construction Diagram

Date/time of construction
Drilling method
Well location (±0.5 ft)
Bore hole diameter
Well depth (±0.05 ft)
Casing material
Screen material
Screen slot size/length
Gravel pack type/size (depths from _____ to _____)
Grout/sealant used (depths from _____ to _____)
Backfill material (depth from _____ to _____)
Surface seal detail (depth from _____ to _____)
Well protector type
Ground surface elevation (±0.01 ft)
Well cap elevation (±0.01 ft)

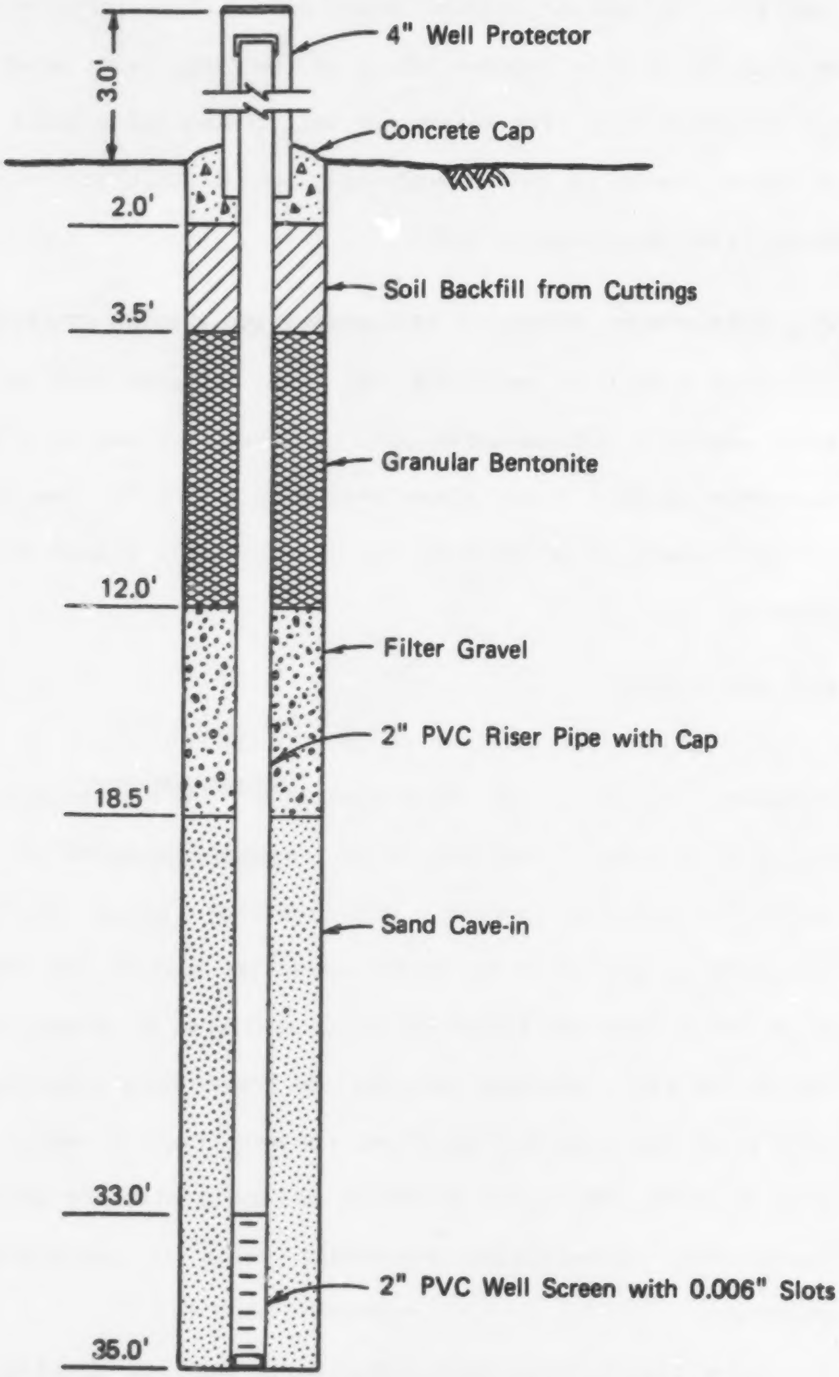

3.0'
4" Well Protector
Concrete Cap
2.0'
Soil Backfill from Cuttings
3.5'
Granular Bentonite
12.0'
Filter Gravel
2" PVC Riser Pipe with Cap
18.5'
Sand Cave-in
33.0'
2" PVC Well Screen with 0.006" Slots
35.0'

Figure 2.11. Monitoring well construction diagram

water level data should indicate the length of time the bore hole was open prior to the water level measurement. This information should not be considered to be representative of the final level water reflected by the finished well. The effects of well trauma and gradual equilibration of water levels in newly-constructed wells limit the value of initial water level measurements (59).

WELL DEVELOPMENT, HYDRAULIC PERFORMANCE AND PURGING STRATEGY

Once a well is completed, the sampling point must be prepared for water sampling and measures must be taken to evaluate its hydraulic characteristics. These steps provide a basis for the maintenance of reliable sampling points over the duration of a ground-water monitoring program.

Well Development

The proper development of monitoring wells is essential to the ultimate collection of "representative" water samples. During the drilling process, fines are forced through the sides of the bore hole into the formation, forming a mud cake that reduces the hydraulic conductivity of the materials in the immediate area of the well bore. To allow water from the formation being monitored to freely enter into the monitoring well, this mud cake must be broken down opposite the screened portion of the well and the fines removed from the well. This process also enhances the yield potential of the monitoring well, a critical factor when constructing monitoring wells in low-yielding geologic materials.

More importantly, monitoring wells must be developed to provide water free of suspended solids for sampling. When sampling for metal ions and other dissolved inorganic constituents, water samples must be filtered and preserved at the well site at the time of sample collection. Improperly developed monitoring wells will produce samples containing suspended sediments that will both bias the chemical analysis of the collected samples and cause frequent clogging of field filtering mechanisms (60). The additional time and money spent for well development will expedite sample filtration and result in samples that are more representative of water chemistry in the formation being monitored.

The development procedure used for monitoring wells are similar to those used for production wells. The first step in development involves the movement of water at alternately high and low velocity into and out of the wellscreened gravel pack to break down the mud pack on the well bore and loosen fines in the materials being monitored. This step is followed by pumping to remove these materials from the well and the immediate area outside the well screen. This procedure should be continued until the water pumped from the well is visually free of suspended materials or sediments.

Techniques for High Hydraulic Conductivity Wells

Successful development methods for relatively productive wells include the use of a surge block, bailing, and surging by pumping. A surge block is a plunger device that fits loosely inside the well casing. It is moved forcibly up and down, causing water to surge in and out of the well screen. After surging, the well must be pumped to remove the fines carried into the well screen and casing. The use of surge blocks for monitoring well development has not been widely used. However, if the surge block is sized to fit loosely in the monitoring well (0.64 cm (1/4 inch) total clearance) it can be operated effectively by hand in relatively shallow wells, less than 15.17 m (50 feet) deep. Care must be taken to avoid damage to the casing or screen when surging a monitoring well.

A bailer also may used to obtain the same surging effect created by a surge block. The bailer must be sufficiently heavy to quickly fall through the water forcing some water to flow out of the well into the surrounding formations. The upward movement of the bailer will then pull the lossened fines into and remove them from the well. The use of bailers for development of monitoring wells is more common than the use of surge blocks. Bailing is generally less effective than using surge block through the potential for well damage is minimized.

Alternately pumping and allowing a well to equilibrate for short intervals is another method for developing monitoring wells. Pumping procedures have had limited application in very high conductivity wells. This is because it is difficult to draw-down these wells sufficiently to create the high entrance velocities necessary for the removal of fines in the aquifer and well bore. This type of development is more often attempted by using air lift pumping mechanisms.

When pumping with air, the effectiveness of the procedure depends on the geometry of the device injecting air into the well. Figure 2.12 illustrates a simple device that diverts air through the well screen to loosen the fines and forces air, water and fines up the well casing and out of the well. This device is particularly effective for developing monitoring wells in very productive geologic materials.

Several important factors should be considered when developing monitoring wells with air. First, the air from the compressor must be

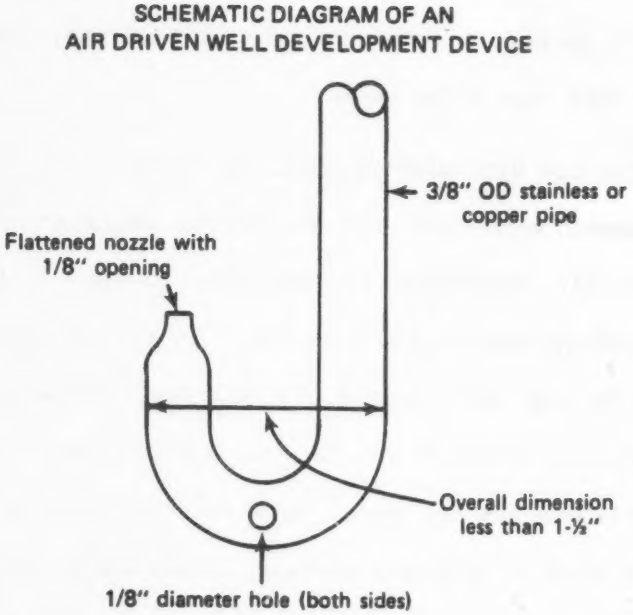

SCHEMATIC DIAGRAM OF AN
AIR DRIVEN WELL DEVELOPMENT DEVICE
3/8" OD stainless or copper pipe
Flattened nozzle with 1/8" opening
Overall dimension less than 1-½"
1/8" diameter hole (both sides)

Figure 2.12

filtered to ensure that oil from the air compressor is not introduced into the well. High volume carbon filters can be used successfully to filter the air from compressors. Secondly, in highly contaminated ground-water situations air development procedures may cause the exposure of field personnel to hazardous materials. Precautions must be taken to minimize personnel exposure. Finally, air development may perturb the oxidation-reduction potential of the formation of interest with effects on the chemistry of initial water samples. Experience shows that in permeable sand and gravel situations, the effects do not persist for more than a few weeks.

Techniques for Low Hydraulic Conductivity Wells

Development procedures for monitoring wells in relatively unproductive geologic materials is somewhat limited. Due to the low hydraulic conductivity of the materials, it is difficult to surge water in and out of the well casing. Also, when the well is pumped, the entrance velocity of water can be too low to remove fines effectively from the well bore and the gravel pack material outside the well screen.

In this type of geologic setting, clean water should be circulated down the well casing out through the screen and gravel pack, and up the open bore hole prior to placement of the grout or seal in the annulus. Relatively high water velocities can be maintained and the mud cake from the bore hole wall will be broken down effectively and removed. Flow rates should be controlled to prevent floating the gravel pack out of the bore hole. Because of the relatively low hydraulic conductivity of geologic materials outside the well, a negligible amount of water will penetrate the formation being monitored. However, immediately following this procedure, the well sealant should be installed and the well pumped to remove as much of the water used in the development process as possible.

Hydraulic Performance of Monitoring Wells

The importance of understanding the hydraulics of the geologic materials at a site cannot be over emphasized. Collection of accurate water level data from properly located and constructed wells provides information on the directions, horizontal and vertical, of ground water flow (61). The success of a monitoring program also depends on knowledge of the rates of travel of both the ground water and solutes. The response of a monitoring well to pumping also must be known to determine the proper rate and length of time of pumping prior to collecting a water sample. Finally, the required sampling frequency should be determined based on the rate of ground-water travel, the mobility and persistence of the chemical constituents of interest, and the goals of the monitoring program.

It is recommended that "field" hydraulic conductivity test be conducted to avoid the unresolved issues involved in laboratory testing. Conductivity tests should be performed on every well in the monitoring system to provide maximum understanding of the hydraulics of the site being monitored, provide information for recommended sampling procedures, and to determine appropriate sampling frequencies for the wells.

Traditionally, hydraulic conductivity testing has been conducted by collecting drill samples which were then taken to the laboratory for testing. Several techniques using laboratory permeameters are routinely used. Falling head or constant head permeameter tests on recompacted samples in fixed wall or triaxial test cells are among the most common. The relative applicability of these techniques is dependent on both operator skill and methodology since calibration standards are not available. The major problem with laboratory test procedures is that one collects data on recompacted geologic samples rather than geologic materials under field conditions. Only limited work has been done to date on performing laboratory tests on "undisturbed" samples to improve the field applicability of laboratory hydraulic conductivity results.

Water Level Measuring Techniques

There are three common water level measurement techniques or devices used for measuring water levels in monitoring wells, steel tapes, electric drop line, and pressure transducers. General descriptions of their use and their relative accuracy are discussed in the following sections.

Steel Tapes

The use of relatively narrow (0.64- to 0.95-cm (1/4- to 3/8-inch) wide) steel tapes is among the most accurate and straight forward methods for making water level measurements. Tapes that are graduated throughout their entire length in feet, tenths of a foot, and hundredths of a foot with raised lettering and divisions are preferable. The raised surface of the tape will permit the observation of color changes when the chalk or other material is wetted. The bottom few feet of the tape is chalked and lowered into the well to the anticipated water level depth so that the chalked portion of the tape is in the water. The tape is held at an even foot mark, making sure that the tape has been continuously lowered into the water and not raised back to the foot marker.

The tape is then withdrawn and the reading from the wetted portion of the tape subtracted from the foot reading held at the measuring point. The resulting value is the depth to water from the measuring point.

Measurements taken in this manner are generally accurate to the nearest 1/100 of a foot. Three readings should be taken for each measurement to ensure that reproducible results are obtained.

Electric Drop Lines

Commercially purchased and home-made drop lines are often used for measuring water levels in monitoring wells. Two conductor electrical wire is fitted with a probe to hold the two wires apart and marked at 30.48- to 152.40-cm (1- to 5-foot) intervals through out its entire length. Drop lines are generally powered by flashlight batteries and equipped with a milliammeter. The drop line is lowered into the well until the probe contacts the water closing the circuit between the two wires and the meter indicates a current flow. The drop line is pulled back and a ruler used to measure the distance between the nearest 30.48- or 152.40-cm (1- or 5-foot) markers on the drop line.

After repeated use the markings on drop lines often have a tendency to become loose or to slide along the wires. Drop lines may also become kinked and don't hang straight in the well. These among other potential problems can limit the accuracy of drop lines to about 1/10 of a foot. They are, however, very convenient to use particularly in deep wells and don't need to be be totally reeled out of the well to get multiple readings.

Pressure Transducers

Pressure transducers have not been used in monitoring wells until the last four to five years. Their use does, however, offer advantages over the steel tape and electric drop line. Transducers can be lowered into a monitoring well to a known distance below the measuring point and by indicating the amount of pressure exerted on it, measures the height of water above the transducer. This amount of "submergence" is subtracted from the depth below the measuring point at which the transducer is located to obtain the depth to the water. Transducers are particularly useful for making water level measurements in a well during pump or slug tests. The transducer is left in the well and transmits a continuous record of water level data to a strip chart or digital recording device during the course of the test. Permanent installations of transducers into individual wells normally cannot be justified because of their relatively high costs.

The accuracy of transducers depends on the type and sensitivity of device used. Most transducers are rated in terms of a percent of their full scale capability. For example, a 0 to 5 psi transducer rated at 0.01 percent will provide readings to the nearest 0.30 cm (0.01 foot). A 0 to 25 psi transducer rated at 0.01 percent will provide reading to the nearest 1.52 cm (0.05 foot).

Hydraulic Conductivity Testing Methods

Slug tests

Slug or bail tests are described in detail in Freeze and Cherry (62). Two tests, one suitable for a point piezometer and one suitable for a well screened over the entire saturated thickness of an aquifer are presented. Both tests are initiated by introducing a sudden change in water level and measuring the resulting response of the well or piezometer. The change in water level can be accomplished by introducing a known quantity of water, slugging the well, or by removing a known quantity of water with a bailer. These methods are suitable for relatively low conductivity settings where the resulting changes in water levels take place slowly and accurate measurements can be made. However, for wells where hazardous contaminants are suspected, removing water from the well may not be desirable. In the case of the slug test, water of a different quality than that in the aquifer also is introduced into the system and must be removed prior to sampling the well.

Prosser (63) described a method of depressing the water level by pressurizing the well casing and then rapidly releasing the pressure to allow the water level to recover. This technique minimizes the disturbance of the well and has the least potential for compromising the integrity of water quality samples. This method also can be used for conducting tests on wells with very high hydraulic conductivities when pressure transducers are used for the water level measurements.

The analyses of slug or bail test data has been described by Hvorslev (64) and Cooper et al. (65). The Hvorslev method is for a point piezometer, while that of Cooper is for a confined aquifer. In most instances the method described by Hvorslev can be used. Hvorslev analysis assumes a homogeneous, isotropic, infinite medium in which both the fluid and soil are incompressible. The rate of inflow to the piezometer (q) is defined by equation 2.3:

$$q(t) = \Pi R^2 (dh/dt) = FK(H - h) \qquad \text{(Eq. 2.3)}$$

where R = radius of the well

F = shape factor determined by the dimensions of the piezometer

K = hydraulic conductivity

H = initial water level above a reference point (±0.01 ft)

h = water level above the reference point at time t (±0.01 ft)

See Figure 2.13a. Hvorslev defines the basic time lag, T_o, as equation 2.4:

$$T_o = (\Pi R^2/FK) \qquad \text{(Eq. 2.4)}$$

By substituting this parameter into equation 1, the solution to the resulting ordinary differential equation, with the initial condition, $h = H_o$ at $t = 0$ is:

$$\frac{H - h}{H - H_o} = e^{-t/T_o}$$

A plot of field recovery data, $H - h / H - H_o$ versus t on a logarithmic scale results in a straight line. Note that for $H - h / H - H_o = 0.37$, $\ln(H - h / H - H_o) = -1$, and from equation 2.4, $T_o = t$. This describes the basic time lag.

To interpret field data, the data are plotted as shown on Figure 2.13b. The basic time lag is graphically measured and K is determined using equation 2.3. For a piezometer intake of length L and radius R, with $L/R > 8$, Hvorslev has evaluated the shape factor, F, and the resulting expression for K is equation 2.5:

$$K = \frac{r^2 \ln(L/R)}{2LT_o} \qquad \text{(Eq. 2.5)}$$

HVORSLEV PIEZOMETER TEST. (a) GEOMETRY; (b) METHOD OF ANALYSIS (from ref. 64)

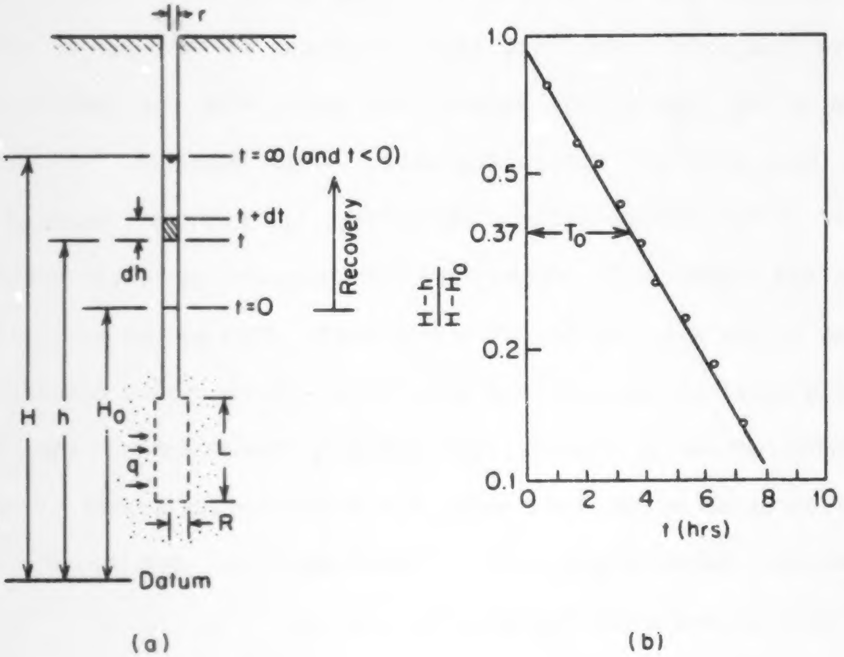

r
t = ∞ (and t < 0)
t + dt
t
dh
t = 0
Recovery
H
h
H_0
q
L
R
Datum
(a)
1.0
0.5
0.37
T_0
0.2
0.1
$\frac{H-h}{H-H_0}$
0
2
4
6
8
10
t (hrs)
(b)

Figure 2.13

Pumping Tests

Pump tests on monitoring wells are often difficult to perform. Relatively low pumping rates, 100 to 1000 milliliters per minute commonly are required to produce data suitable for analysis. Problems of disposing of the water pumped and making accurate water level readings also must be addressed. Constant rate pump tests for periods of two to four hours are normally required. Traditional analyses of pump test data use equations derived by Theis (66) and Jacob (67). One of the basic assumptions made in deriving those equations is that all of water pumped from a well during the pumping test comes from the aquifer and none comes from storage within the well. This condition is seldom encountered in monitoring wells. Therefore, the methods presented by Papadopulos and Cooper (68), which take into account the water removed from storage in the well casing, should be used. This method as applied to monitoring wells is described by Gibb (11). It should be noted that the well construction procedures, particularly "smearing" of the well bore or infiltration of drilling muds, can significantly impact hydraulic conductivity calculations (69). Therefore, well development is essential prior to hydraulic conductivity testing.

Analysis of Water Level Data

In settings where slug tests or pump tests can not be performed, historical water level data can be analyzed using the procedures outlined by Stallman (70). Reasonable estimates of hydraulic conductivity can be made by selecting appropriate well arrays and periods of time when little or no recharge has occurred. Successive selections of various well arrays will permit the determination of hydraulic conductivity values for most wells in a monitoring program.

In all of the above described procedures there are significant sources of error. Water levels should be measured to the nearest ±0.30 centimeters (0.01 foot),flow rates for pump tests to ±5 mL per minute, and time to the nearest 2 seconds. Hydraulic conductivity values determined by the various methods should not be considered to be more precise than ±20 percent. To minimize the potential error and quantify the degree of variance, 3 to 5 slug or pressure tests should be conducted on each well. The time and expense required to perform multiple pump tests do not normally warrant the effort.

In addition to the above sources of measurement and interpretive errors, wells that have not been properly constructed or developed will not provide accurate data for determining hydraulic conductivity values of the materials in which the well is finished. Care also must be exercised when performing these tests to insure that pumping or injection of water by nearby wells does not affect the results of these tests.

Well Maintenance Procedures

A plan for well maintenance and performance reevaluation should be prepared to insure that the sampling point remains reliable. As a minimum, high and low water level data periods for the site should be examined once every two years to insure that the well locations (horizontally and vertically) are still acceptable. It is also particularly important to note that the exposure of the screened interval to the atmosphere due to low water levels can compromise the integrity of water samples. Hydraulic conductivity tests should be performed once every five years or whenever significant amounts [7.62-15.24 cm (0.25-0.50 feet)] of sediment have accumulated in the well. Deficiencies in well locations, delivery of decreases in hydraulic conductivity, or turbid samples should be corrected by well redevelopment, the installation of new wells or the rehabilitation of existing wells.

The operation of wells in the vicinity of the site under investigation also may affect changes in the hydrologic setting and resulting flow paths. Biannual evaluation of the high and low water level conditions at a site under evaluation is recommended to ensure that the well locations and depths are still appropriate. Piezometric surface maps for horizontal flow direction determination and vertical cross sections of equipotential lines for vertical flow determination should be plotted and reviewed. The example below illustrates how site operation often causes failure of the original monitoring well design.

Example 2.2. Effects of waste disposal activities on site flow regime--

Figure 2.14 showed a relatively flat site with a slight water table gradient prior to the placement of a waste impoundment. Background and down gradient wells were constructed to determine the hydrologic and chemical nature of the site prior to waste disposal. Water level data from the nested monitoring wells were used to determine the horizontal and vertical components of ground-water flow. In the pre-disposal situation water passing the upgradient shallow well BG-S was expected to flow past the deep downgradient well DG-D2.

After the installation of the disposal system a ground-water mound was created beneath the impoundment. The increased head beneath the impoundment also resulted in the reversal of ground-water flow in its immediate vicinity. Background wells BG-D and BG-S are both now likely to receive leachate from the source. Similarly, the increased head beneath the impoundment increases the vertical component of flow and causes the downgradient flow of ground water to move deeper into the regional flow system. This shift in flow patterns indicates the need to construct a deeper well at the site DG-D2 and DG-S2.

This type of analysis should be performed for high and low water level periods once every two or three years to insure that the designed monitoring system is still applicable to possible changes in the hydrologic system.

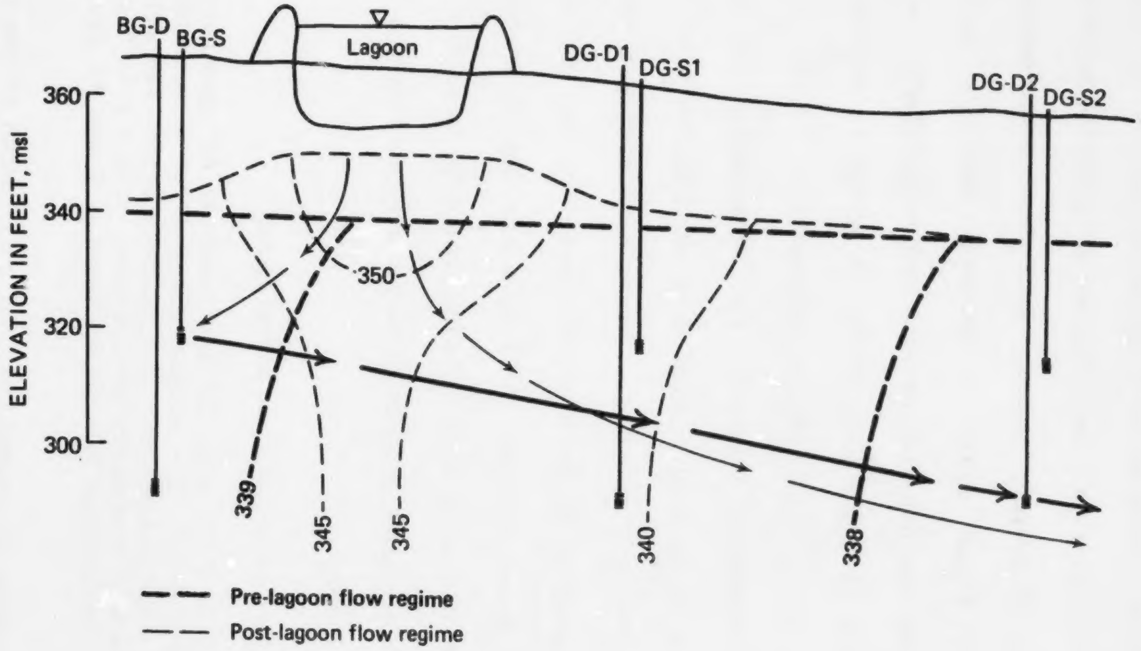

BG-D
BG-S
Lagoon
DG-D1
DG-S1
DG-D2
DG-S2
360
340
320
300
ELEVATION IN FEET, msl
350
339
345
345
340
338
Pre-lagoon flow regime
Post-lagoon flow regime

Figure 2.14. Effects of waste-handling activity on ground-water flow paths

In addition to determining that the monitoring wells are still properly located, documentation must be presented to ensure that the wells are physically intact and capable of yielding water samples as designed. Chemical encrustation or bacterial growths on the well screen may result in decreased well performance and possible alteration of the chemical quality of pumped samples. Well depth measurements should be reported on an annual basis to document that the well is still physically intact and not filling with sediment. Turbid water samples are an indication that the well intake or screen is not functioning as designed and is likely to accumulate sediments.

Another recommended procedure for documenting the integrity of monitoring wells is to require that slug or pump tests be conducted on each well once every five years. Comparisons of these test data with thatcollected originally provides documentation on the presence and degree of well deterioration. This data can then be used to determine if and when new wells or well rehabilitation is needed. The example below illustrates common problems often encountered as the age of monitoring wells increase.

Example 2.3. Well deterioration and plugging--

A thirty-five foot deep, 2-inch diameter PVC monitoring well was installed in September 1979 within 250 feet of a petrochemical plant waste disposal impoupndment site. Upon completion, the well was tested and found to have a hydraulic conductivity of 5.2×10^{-4} cm/sec. Non-pumping water levels have fluctuated between 5 and 12 feet below land surface.

As per recommended procedures, the total depth of the well has been measured once a year. During the first two years, sediment accumulations of 0.50 and 0.38 feet were measured, respectively. During the next three years, no accumulated sediment was found. After five years of operation, another hydraulic conductivity test was performed on the well. Data revealed that the conductivity had dropped to 3.7×10^{-6} cm/sec.

The problems associated with this well are two-fold. During the first two years, sediment had accumulated due to improper development procedures. The cessation of sediment accumulation could have been due to the ultimate development of the well from repeated pumping during the sampling of the well. It also could have been due to the slow plugging of the well screen or aquifer reflected by the drop in hydraulic conductivity. Due to the nature of the possible leachate from the disposal site being monitored, the life of the well could be threatened by attack of the well casing materials. Careful monitoring of the well performance and chemistry is recommended. The well may need to be replaced with a new well constructed of more suitable materials for this type of environment.

Well Purging Strategies

The number of well volumes to be pumped from a monitoring well prior to the collection of a water sample must be tailored to the hydraulic properties of the geologic materials being monitored, the well construction parameters, the desired pumping rate, and the sampling methodology to be employed. There is no one single number of well volumes to be pumped that is best or fits all situations. The goal in establishing a well purging strategy is to obtain water from the geologic materials being monitored while minimizing the disturbance of the regional flow system and the collected sample. To accomplish this goal a basic understanding of well hydraulics and the effects of pumping on the quality of water samples is essential. Water that has remained in the well casing for extended periods of time (i.e. more than about two hours) has the opportunity to exchange gases with the atmosphere and to interact with the well casing material. The chemistry of water stored in the well casing is unrepresentative of that in the aquifer and it should not be collected for analysis. Purge volumes and pumping rates should be evaluated on a case by case basis.

Pumping Rates

The rate at which wells are purged of stagnant water should be kept to a minimum. Purging rates should be maintained below the rates at which well development was performed since well damage can result. High purging rates can also cause additional development to occur with resulting increased turbidity of water samples. Well hydraulic performance evaluation is essential to the determination of effective well purching rates and volume requirements.

Evaluation of Purging Requirements

When a well is pumped a certain amount of drawdown is created in the well and the surrounding aquifer system to induce flow of water to the well. Traditional well analysis techniques described by Theis (66) and Jacob (67) can be used to predict the amount of drawdown experienced by wells under water table and piezometer conditions. The reader should recall from above that the basic assumptions made in deriving these relationships require that an insignificant amount of the water pumped comes from the well bore. This condition is seldom experienced in the case of small diameter monitoring wells, particularly for wells finished in low hydraulic conductivity geologic settings. Popadopulos and Cooper (68) presented an equation that describes the discharge from a pumped well which takes into account the volume of water removed from casing storage.

Well test data for six monitoring wells studied in Illinois have been analyzed using these equations (11). At all of the sites studied,, the nonpumping water levels were significantly above the top of the aquifers tapped, suggesting artesian conditions. In this case, a storage coefficient of 0.0001 was used in the analysis of the drawdown data. The storage coefficient values selected should have little effect on the predicted drawdowns for most aquifer systems using this equation.

Using the Popadopulos and Cooper equations (68), the percentages of aquifer water pumped for a two inch diameter well pumping at a rate of 500 mL/min for a range of transmissivities were calculated, see Figure 2.15. These calculations give an indication of the sources of water at various times for a well that is being pumped with the pump intake at the top of the well screen. Different percentages would result if the pumping rate, well diameter, or aquifer properties were different. These types of calculations should be used as guidelines for the selection of the appropriate pumping rate and numbers of well volumes to be pumped prior to sample collection. However, they are only guidelines and should be verified by the measurement of indicator parameters at the well head during pumping collection. Two examples of pumping rate selection and appropriate well purging volumes are given below.

Example 2.4. Well purging strategy based on hydraulic conductivity data--

Given:

48-foot deep, 2-inch diameter well
2-foot long screen
3-foot thick aquifer
static water level about 15 feet below land surface
hydraulic conductivity = 10^{-2} cm/sec

Assumptions:

A desired purge rate of 500 mL/min and sampling rate of 100 mL/min will be used.

Calculations:

One well volume = (48 ft - 15 ft) x 613 mL/ft (2-inch diame well)
= 20.2 liters

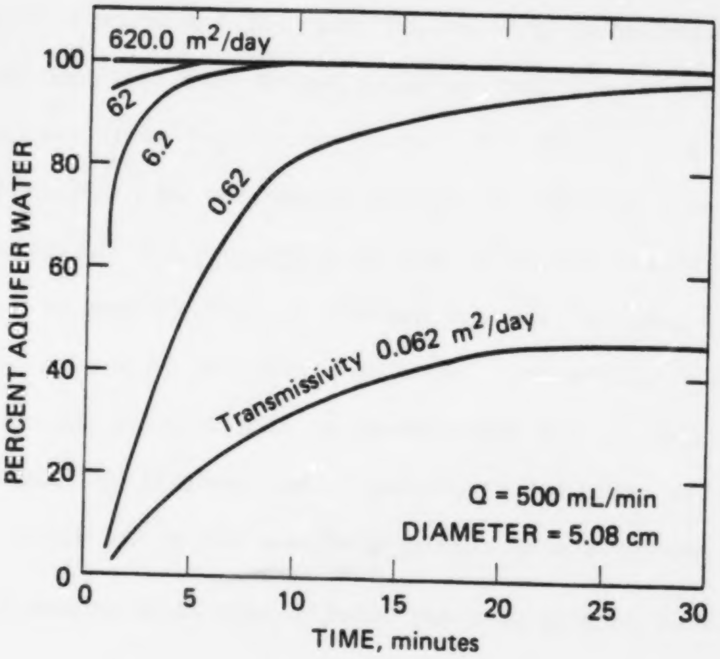


Figure 2.15. Percentage of aquifer water versus time for different transmissitivites

Aquifer Transmissivity = hydraulic conductivity x aquifer thickness
= 10^{-4} m/sec x 1 meter
= 10^{-4} m^2/sec or 8.64 m^2/day

From Figure 2.15

at 5 minutes ~95% aquifer water and
(5 min x 0.5 L/min)/20.2 L
0.12 well volumes
at 10 minutes ~100% aquifer water and
(10 min x 0.5 L/min)/20.2 L
= 0.24 well volumes

It therefore appears that a high percentage of aquifer water can be obtained within a relatively short time of pumping. The indicator parameters should be monitored and the pumping rate slowed to the desired 100 mL/min for sampling as soon as they have stabilized. The indicator parameters should be monitored at very close intervals, every 1 or 2 minutes from the time pumping begins.

Example 2.5. Well purging strategy based on hydraulic conductivity data--

Given:

48-foot deep, 2-inch diameter well
2-foot long screen
3-foot thick aquifer
static water level about 15 feet below land surface
hydraulic conductivity = 10^{-4} cm/sec

Assumptions:

A desired purge rate of 500 mL/min and sampling rate of 100 mL/min will be used.

Calculations:

One well volume = (48 ft - 15 ft) x 613 mL/ft (2-inch diameter well)
= 20.2 liters

Aquifer Transmissivity = hydraulic conductivity x aquifer thickness
= 10^{-6} m/sec x 1 meter
= 10^{-6} m^2/sec or 0.0864 m^2/day

From Figure 2.15

at 5 minutes ~20% aquifer water and
(5 min x 0.5 L/min)/20.2 L
~0.12 well volumes
at 10 minutes ~30% aquifer water and
(30 min x 0.5 L/min)/20.2 L
~0.72 well volumes

Based on these results, it appears that it may be more desirable to pump this well down to the top of the screen and allow it to recover. Dewatering the screen and the gravel pack should be avoided to minimize aeration effects on water chemistry. The samples can then be collected at the desired 100 mL/min while the well is recovering. Calculations using the equations developed by Papadopulos and Cooper suggest that the well should recover at a rate of about 250 mL/min when the water level is near the top of the screen. Therefore, the samples can be collected within five minutes after dewatering pumping stops and can continue until the desired volume of sample is collected.

If the well was not capable of recovering at a rate in excess of 100 mL/min, the sample would have to be collected in small aliquots. The amount of water that could recover in two hours should be collected and another recovery period would be required to collect the next sample segment. The recovered water should not be allowed to remain in the well casing for more than about two hours prior to collection or it is likely to be chemically altered for several parameters.

The selection of purging rates and volumes of water to be pumped prior to sample collection can also be influenced by the anticipated water quality. In hazardous environments where purged water must be contained and disposed of in a permitted facility, it is desirable to minimize the amount of purged water. This can be accomplished by pumping the wells at very low pumping rates (100 mL/min) to minimize the drawdown in the well and maximize the percent aquifer water delivered to the surface in the shortest period of time. Pumping at low rates, in affect, isolates the column of stagnant water in the well bore and negates the need for its removal. This approach is only valid in cases where the pump intake is placed at the top of, or in, the well screen.

In summary, well purging strategies should be established by 1) determining the hydraulic performance of the well; 2) calculating reasonable purging requirements, pumping rates, and volumes based on hydraulic conductivity data, well construction data, site hydrologic conditions, and anticipated water quality; 3) measuring the well purging parameters to verify chemical "equilibrated" conditions; and 4) documenting the entire effort (actual pumping rate, volumes pumped, and purging parameter measurements before and after sample collection).

SAMPLING MECHANISMS AND MATERIALS

The selection of appropriate sampling mechanisms and materials are vital to the success of any ground-water investigation. A situation may be very thoroughly evaluated as to the hydrogeologic conditions, optimized sampling frequency and analyte selection. Also, the sampling points may be constructed and evaluated properly. Nonetheless, if poor sampling mechanisms and materials are incorporated into the program, all the preceding effort may be futile. Minimally disturbed samples must be carefully collected and analyzed if the program is to meet its information needs. In many cases, the results of preliminary investigations can be reinterpreted, even if inappropriate choices of sampling mechanisms or materials have been used prior to the execution of a sampling experiment. These experiments should include simultaneous sample collection by both the previous mechanism and sampling components, as well as those which are more appropriate for the current situation based on the available data. For example, an initial set of monitoring results collected with a conventional bailer may show a trace of volatile organic contaminants. In order to substantiate these observations and improve the reliability of the results, a sampling experiment should be run, including both bailed and bladder pumped samples on at least two successive sampling dates. This approach will permit the objective evaluation of the effect of sampling procedures on the quality of the results and hopefully will put an end to the generation of poor data. Tradition is a very weak basis for the selection or continued use of inappropriate mechanisms or materials.

Sampling Mechanisms

Sampling mechanisms for the collection of ground-water samples are among the most error prone elements of monitoring programs. Several useful sources have reviewed the range of available sampler designs and should be consulted for specific information (3,11,13,52,71,72). Unfortunately, the documentation of field sampling performance for many of the available devices is lacking. Many of the sampling designs may be expected to provide adequate performance for conservative chemical constituents which are not (or minimally) affected by aeration, gas-exchange and degassing. Among these constituents are Na^+, K^+ and Cl^-. The chemical constituents which can provide the most useful information to the investigation frequently are effected by the improper choice of sampling mechanisms. Evaluations of sampling performance based on the recovery of conservative, unreactive chemical constituents are simply not reliable for planning effective monitoring efforts.

The introduction of bias into ground-water data sets by sampling mechanisms has been investigated by several groups (13,53). In a controlled laboratory evaluation (53), results disclosed that sampling for dissolved gases or volatile organic compounds is prone to severe negative bias of the same order as analytical error. Further, the precision which may be achieved in these cases is limited by both operator skill and sampler design. The magnitude of these errors corresponded to the extent to which control over conditions during sample transfer steps (i.e. flow rate, atmospheric exposure, turbulence) could be maintained. Positive displacement bladder pumps were found to be the most reliable sampling mechanism evaluated since they are simple in design and operation and operational variables are easily controlled.

Similarly, Korte and Kearl (73) recommended positive displacement bladder pumps over bailers, suction-lift and air-lift devices due to the bladder pumps' range of utility, minimal disturbance of the samples and overall simplicity of operation. They also noted that bladder pumps permit efficient in-line filtration of samples in the field.

Modifications of selected sample collection mechanisms are being developed to improve the reliability and applicability of ground-water chemical data. Armstrong and McLaren (74) have refined pump/packer arrangements to optimize the isolation of the sample intake as well as sample recovery. Pankow et al. (40) have investigated the application of in situ sample collection techniques for organic compounds which have the advantage of minimizing sample exposure to either the atmosphere or foreign materials. The routine application of these and other refinements for ground-water sampling efforts (75) must await further development.

Work to date has established that there is a great need for the field evaluation of sampling mechanisms. This work has also identified the capabilities which a reliable sampling mechanism should provide .

Important characteristics of ground-water sampling devices which should be considered are:

1. The devices should be simple to operate in order to minimize the possibility of operator error.
2. The device should be rugged, portable, cleanable and repairable in the field.
3. The device should have good flow controllability to permit low flow rates (≦100 mL/min) for sampling volatile chemical constituents, as well as high flow rates (>1 L/min) for large-volume samples and purging stored water from monitoring wells.
4. The mechanism should minimize the physical and chemical disturbance of ground-water solution composition in order to avoid bias or imprecision in analytical results.

The scientific literature is somewhat inconsistent in descriptions of the types of samplers and their primary mechanisms of operation. In this regard, *gas-lift mechanisms* are exemplified by down-hole dual tube arrangements, which employ violent gas/water mixing to force water up and out of the well bore (or large diameter tube). *Gas lift devices* are *proven* to be *biased sampling mechanisms* for a range of chemical constituents. They are *not recommended* for *any type* of *ground-water investigation*. *Gas-drive devices*, on the other hand, rely on controlled displacement of water from the sampler body by either controlled gas pressure applied across an interface or by gas pressure on a membrane which permits for no gas contact with the sample.

Many sampling devices are designed for either deployment in a well bore or as devices which are buried at discrete depths, gravel/sand packed and sealed from other formations analogous to a properly completed screened interval in conventional wells. There are advantages to the use of dedicated samplers, particularly for complex monitoring situations which demand large arrays of sampling points. The corresponding disadvantages include difficulties in assessing proper placement or malfunction. The collection of hydrologic data is severely limited by most of these devices. The choice of a sampler design, appropriate for the situation of interest, should be made carefully after a comprehensive review of the scientific literature.

Recommendations for Selecting Sampling Mechanisms

It should be recognized that [illegible] purchase of a suitable sampler for most ground-water investigations is usually a very small portion of the overall program cost. It is further obvious that the choice of the right sampler will determine the usefulness of the chemical data. A sensible approach is to make the choice of a sampler on the basis of the most troublesome parameters which may be of interest. Typically, samples for dissolved gases and volatile organic compounds are the most difficult to collect and handle.

Negative bias (loss of constituent) is the most common reason for poor sampling performance for gas-sensitive or volatile compounds. In general, sampling precision may be poorer by a factor of two or more than that involved in analytical methodologies alone. Sampling bias problems may be far worse under field conditions, particularly for suction mechanisms and those devices which involve careful operator attention or control (e.g. bailers and gas drive devices). Positive displacement bladder pumps meet all of the important characteristics for sampling mechanisms noted above. These pumps have been found to be very reliable, efficient sampling mechanisms which exhibit excellent overall performance in all reported evaluations to date.

Table 2.4 contains general recommendations for ground-water sampling mechanisms. It should be noted that it is the responsibility of the monitoring program director to build in sampling performance checks into the QA/QC program to verify actual efficiency for the chemical constituents of interest.

Sampling Materials

There exists a wide range of biological, chemical and hydrologic conditions which may be encountered in ground-water sampling programs. Even if personnel safety is assured, ground-water sampling activities must be approached cautiously. There are many chemical and physical unknowns which must be accounted for, if the monitoring data is to be truly useful. Sampling mechanisms are only an element of sampling protocols, the materials which contact the samples must be chosen carefully as well.

Subsurface Conditions and Materials' Effects

The "Guide to the Selection of Materials for Monitoring Well Construction and Ground-Water Sampling" (52) and the thorough treatment of sources of sampling bias by Gillham, et al. (13) provide very useful recommendations for materials' selection and error minimization for ground-water investigations. Both of these publications review the potential obstacles to materials' related error control.

Well casing materials, well construction and completion procedures and sample handling precautions all enter into the ultimate quality of

Table 2.4. Performance Evaluation of Ground-Water Sampling Mechanisms (ref. 53)

Mechanism category	Overall performance ranking	Remarks
Positive displacement (bladder)	Above average	Expected to provide both efficient well purging and representative samples over a range of conditions with minimal difficulty in field operations.
Grab samplers (conventional bailer) (dual-check valve bailer) (syringe pump)	 Average Average Average--below average	Unsuitable for well purging; require very careful operation and sample handling precautions under field conditions; field performance open to question.
Positive displacement (mechanical)	Average--below average	Suitable for well purging; sampling performance very dependent on specific design and operational details.
Gas displacement (gas drive; not gas lift)	Average--below average	May be suitable for well purging if used in conventional installations; malfunctions are difficult to assess or repair; significantly lower recoveries of purgeable organic compounds and gases may occur depending on field conditions and operator experience.
Suction (peristaltic)	Below average	Suitable for well purging at depths to approximately 20 feet; significantly lower recoveries of purgeable organic compounds and gases will result from sampling with this mechanism.

ground-water data. The principal processes by which materials can effect chemical data are:

chemical attack: corrosion/deterioration
microbial colonization, attack
sorption effects: adsorption/absorption
leaching effects: matrix/sorbed component release

These processes may lead to the observation of false trends in analyte concentrations, highly variable water chemistry and the identification of artefacts resultant from surface release or sorptive interactions. As with the errors which sampling mechanisms can introduce into the chemical data, materials' related errors can be quite significant and difficult to predict (23,52). Appropriate materials' choice for each application must be made on the basis of long-term durability, cleanability, and the minimization of the secondary effects of sorption or leaching. Structural integrity is, therefore, the primary criterion for making reliable material choices. The materials must neither be attacked nor degraded during the course of the monitoring program. Then the severity of the effects of loss or contamination resulting from sorption or leaching of the components of the sampling train must be considered. In general, it is wise to base materials' choices on the most error prone constituents of interest.

To evaluate the magnitude of materials' effects, it is instructive to consider the relative surface area contact which aquifer solids, well casing and sampling tubing will have with the water samples. Table 2.5 contains a comparison of these materials and their relative surface area contact under monitoring well sampling conditions. Assuming relatively high linear ground-water velocity (50 $cm \cdot d^{-1}$) and pumping rates of ~100 mL/min, it follows that aquifer solids are a potentially

Table 2.5. Relative Sample Contact Comparison for Selected Materials

Solid	A surface area	V volume (porosity)	A/V $(m^2 \cdot L^{-1})$	Flow rate $(L \cdot hr^{-1})$	Areal contact rate $(m^2 \cdot hr^{-1})$	Relative surface contact*
AQUIFER SOLIDS sand ($U = 50\ cm \cdot d^{-1}$)	25 m^2/g	(50) %	6.3×10^4	1.04×10^{-3}	66	92
WELL CASING 2" O.D.	0.06 m^2/ft	0.5 L/ft	0.12	6	0.72	1
SAMPLING TUBING 1/4" O.D.	0.006 m^2/ft	0.009 L/ft	0.67	6	4.0	6

* Normalized to well casing value of areal contact rate

greater source of material surface effects on water quality than either well casing or sampling tubing. Since we cannot exert control over the native geology, the effects of gravel packs and grouting materials may be expected to be more important than those due to well casing or sampling train materials. Relative to conditions in the geologic formation of interest, sampling tubing is in much more intimate contact with the water sample collected after proper purging than would be the well casing. One should not assume that materials' effects will cancel out in comparisons of upgradient or downgradient monitoring well data. Materials' related bias will be present in all samples though perhaps not to the same extent. The effects of materials in comparisons of sample results are most pronounced under differing chemical conditions where some materials may be attacked or leached to varying degrees. Purging may minimize the effects of potential well casing interferences, however this is difficult to substantiate under field conditions.

Sampling train components, particularly sampling tubing, are the most critical selections which must be made to avoid materials' related error. A recent study has demonstrated that serious bias of dissolved organic compound results occurs quite rapidly (within 5-10 minutes) due to absorption on flexible tubing exposures (76). In this study all commonly used tubing materials (Teflon$^{(R)}$, polypropylene, polyethylene, etc.) sorbed organic compounds to some extent. The sorptive error was most serious for polyvinyl chloride and silicone rubber tubing.

Recommendations for Selecting Sampling Materials

The primary criteria for the selection of materials for all components of the sampling point and sample collection train should be mechanical performance and chemical inertness. Since the actual subsurface geologic and chemical conditions which may be encountered are very difficult to predict, the choice of materials must be made carefully. It is recommended that sampling components be chosen of the most inert and error-free materials available. The costs of analysis (or repeat analyses) and the labor involved in sample collection are generally much higher than the cost of appropriate materials for sampling ground water.

Sampling materials may be categorized as either rigid or flexible. Rigid components include well casing, pump bodies and fittings, while tubing, bladders and gaskets are generally flexible materials. Tables 2.6 and 2.7 detail general recommendations for rigid and flexible materials, respectively. Teflon(R) components are superior to all other materials' combinations for ground-water sampling. The mechanical performance of this material may require that it be used in combination with stainless steel. The available literature on materials evaluation for sampling ground water substantiates these recommendations (23,52, 72,76).

SAMPLE COLLECTION PROTOCOL

A well conceived sampling protocol consists of a written description of the actual sampling and analytical procedures involved in obtaining representative ground-water data. The protocol must reflect special attention to the need to collect high quality hydrologic data (e.g. water level, hydraulic conductivity, etc.) and to record any unusual occurrences or departures from written procedures. The value of water quality measurements has been emphasized repeatedly in the literature. However, it is very difficult to fully interpret the water

Table 2.6. Recommendations for Rigid Materials in Sampling Applications (In decreasing order of preference)

Material	Recommendations
Teflon(R) (flush threaded)	Recommended for most monitoring situations with detailed organic analytical needs, particularly for aggressive, organic leachate impacted hydrogeologic conditions. Virtually an ideal material for corrosive situations where inorganic contaminants are of interest.
Stainless Steel 316 (flush threaded)	Recommended for most monitoring situations with detailed organic analytical needs, particularly for aggressive, organic leachate impacted hydrogeologic conditions.
Stainless Steel 304 (flush threaded)	May be prone to slow pitting corrosion in contact with acidic high total dissolved solids aqueous solutions. Corrosion products limited mainly to Fe and possibly Cr and Ni.
PVC (flush threaded) other noncemented connections, only NSF* approved materials for well casing or potable water applications	Recommended for limited monitoring situations where inorganic contaminants are of interest and it is known that aggressive organic leachate mixtures will not be contacted. Cemented installations have caused documented interferences. The potential for interaction and interferences from PVC well casing in contact with aggressive aqueous organic mixtures is difficult to predict. PVC is not recommended for detailed organic analytical schemes.
	Recommended for monitoring inorganic contaminants in corrosive, acidic inorganic situations. May release Sn or Sb compounds from the original heat stabilizers in the formulation after long exposures.

(R) Trademark of DuPont, Inc.

* National Sanitation Foundation approved materials carry the NSF logo indicative of the product's certification of meeting industry standards for performance and formulation purity.

Table 2.6. (Continued)

Material	Recommendations
Low-Carbon Steel Galvanized Steel Carbon Steel	May be superior to PVC for exposures to aggressive aqueous organic mixtures. These materials must be very carefully cleaned to remove oily manufacturing residues. Corrosion is likely in high dissolved solids acidic environments, particularly when sulfides are present. Products of corrosion are mainly Fe and Mn, except for galvanized steel which may release Zn and Cd. Weathered steel surfaces present very active adsorption sites for trace organic and inorganic chemical species.

Table 2.7. Recommendations for Flexible Materials in Sampling Applications (In decreasing order of preference)

Materials	Recommendations
Teflon(R)	Recommended for most monitoring work, particularly for detailed organic analytical schemes. The material least likely to introduce significant sampling bias or imprecision. The easiest material to clean in order to prevent cross-contamination.
Polypropylene	Strongly recommended for corrosive high dissolved solids solutions. Less likely to introduce significant bias into analytical results than polymer formulations (PVC) or other flexible materials with the exception of Teflon(R).
Polyethylene (linear)	
PVC (flexible)	Not recommended for detailed organic analytical schemes. Plasticizers and stabilizers make up a sizable percentage of the material by weight as long as it remains flexible. Documented interferences are likely with several priority pollutant classes.
Viton(R)	Flexible elastomeric materials for gaskets, O-rings, bladder and tubing applications. Performance expected to be a function of exposure type and the order of chemical resistance as shown. Recommended only when a more suitable material is not available for the specific use. Actual controlled exposure trials may be useful in assessing the potential for analytical bias.
Silicone (medical grade only)	
Neoprene	

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chemistry or the actual extent of contamination unless high quality hydrologic data is collected and interpreted properly. Indeed, it may be advisable to collect the hydrologic data at more frequent intervals and at finer spatial scale than that used for the chemical data.

The principal steps in the sampling protocol are listed in Figure 2.16. The goal for each step is also provided with a general recommendation for achieving it. These general elements are common to all ground-water sampling efforts. It should be the responsibility of a designated member of the sampling staff to record progress through the protocol at each sampling point.

To insure maximum utility of the sampling effort and resulting data, documentation of the sampling protocol as performed in the field is essential. In addition to noting the obvious information (i.e., persons conducting the sampling, equipment used, weather conditions, and documentation of adherence to the protocol and unusual observations) three basic elements of the sampling protocol should be recorded: 1) water level measurements made prior to sampling, 2) the volume and rate at which water is removed from the well prior to sample collection (well purging), and 3) the actual sample collection including measurement of well-purging parameters, sample preservation, sample handling and chain of custody.

Water Level Measurement

Prior to the purging of a well or sample collection, it is extremely important to measure and record the water level in the well to be sampled. Water level measurements are needed to estimate the amount of water to be pumped from the well prior to sample collection. In

Step	Goal	Recommendations
Hydrologic Measurements	Establish nonpumping water level.	Measure the water level to ±0.3 cm (±0.01 ft).
Well Purging	Removal or isolation of stagnant H_2O which would otherwise bias representative sample.	Pump water until well purging parameters (e.g., pH, T, Ω^{-1}, Eh) stabilize to ±10% over at least two successive well volumes pumped.
Sample Collection	Collection of samples at land surface or in well-bore with minimal disturbance of sample chemistry.	Pumping rates should be limited to ~100 mL/min for volatile organics and gas-sensitive parameters.
Filtration/ Preservation	Filtration permits determination of soluble constituents and is a form of preservation. It should be done in the field as soon as possible after collection.	Filter: Trace metals, inorganic anions/cations, alkalinity. Do not Filter: TOC, TOX, volatile organic compound samples; other organic compound samples only when required.
Field Determinations	Field analyses of samples will effectively avoid bias in determinations of parameters/constituents which do not store well: e.g., gases, alkalinity, pH.	Samples for determinations of gases, alkalinity and pH should be analyzed in the field if at all at all possible.
Field Blanks/ Standards	These blanks and standards will permit the correction of analytical results for changes which may occur after sample collection: preservation, storage, and transport.	At least one blank and one standard for each sensitive parameter should be made up in the field on each day of sampling. Spiked samples are also recommended for good QA/QC.
Sampling Storage/ Transport	Refrigeration and protection of samples should minimize the chemical alteration of samples prior to analysis.	Observe maximum sample holding or storage periods recommended by the Agency. Documentation of actual holding periods should be carefully performed.

Figure 2.16. Generalized ground-water sampling protocol

addition, this information can be useful when interpreting monitoring results. Low water levels may reflect the influence of a nearby production well. High water levels compared to measurements made at other times of the year are indicative of recent recharge events. In relatively shallow monitoring settings high water levels from recent natural recharge events may result in dilution of the total dissolved solids in the collected sample. Conversely, if contaminants are temporarily held in an unsaturated zone above the geologic zone being monitored, recharge events may "flush" these contaminants in the shallow ground water system and result in higher levels of some constituents.

Documenting the nonpumping water levels for all wells at a site will provide historical information on the hydraulic conditions at the site. Analysis of this information will reveal changes in flow paths and serve as a check on the effectiveness of the wells to monitor changing hydrologic conditions. This information is also essential to develop an understanding of the seasonal changes in water levels and associated chemical concentration variability at the monitored site.

Purging

The volume of stagnant water which should be removed from the monitoring well should be calculated from the analysis of field hydraulic conductivity measurements. Rule of thumb guidelines for the volume of water which should be removed from a monitoring well prior to sample collection ignore the actual hydraulic performance of the sampling point. These 3-, 5- or 10-well volume purging guidelines are a liability in time, expense and information return from the sampling activities.

The calculated well purging requirement should also be monitored in the field by the in-line monitoring of the well purging parameters (e.g. Eh, pH, T, and Ω^{-1}). In-line measurements provide the most representative data for these constituents and verify the reliability of the hydraulic evaluation of the sampling point or well (2,77). These chemical constituents further aid in the interpretation of water quality changes as they are affected by hydrologic conditions. Modifications to the electrode cell in these flow-through instruments have resulted in their improved performance in the field (78). A photograph of this instrument is provided in Figure 2.17.

For example, the calculated well purging requirement (e.g. >90% aquifer water) calls for the removal of five well volumes prior to sample collection for a particular well. Field measurements of the well purging parameters have historically confirmed this recommended procedure. During a subsequent sampling effort, twelve well volumes were pumped before stabilized well purging parameter readings were obtained. Several possible causes could be explored: 1) A limited plume of contaminants may have been present at the well at the beginning of sampling and inadvertently discarded while pumping in an attempt to obtain stabilized indicator parameter readings; 2) The hydraulic properties of the well have changed due to silting or encrustation of the screen indicating the need for well rehabilitation or maintenance; 3) The flow through device used for measuring the indicator parameters was malfunctioning; or 4) The well may have been tampered with by the introduction of a contaminant or relatively clean water source in an attempt to bias the sample results.

Documentation of the actual well purging process employed should be a part of a standard field sampling protocol. Figure 2.18 presents a one-page form which may be used for documenting field sampling operations at each sampling point.

Sample Collection

The initial hydrologic and well purging measurements necessary for reliable ground-water sampling should be entered into the same field

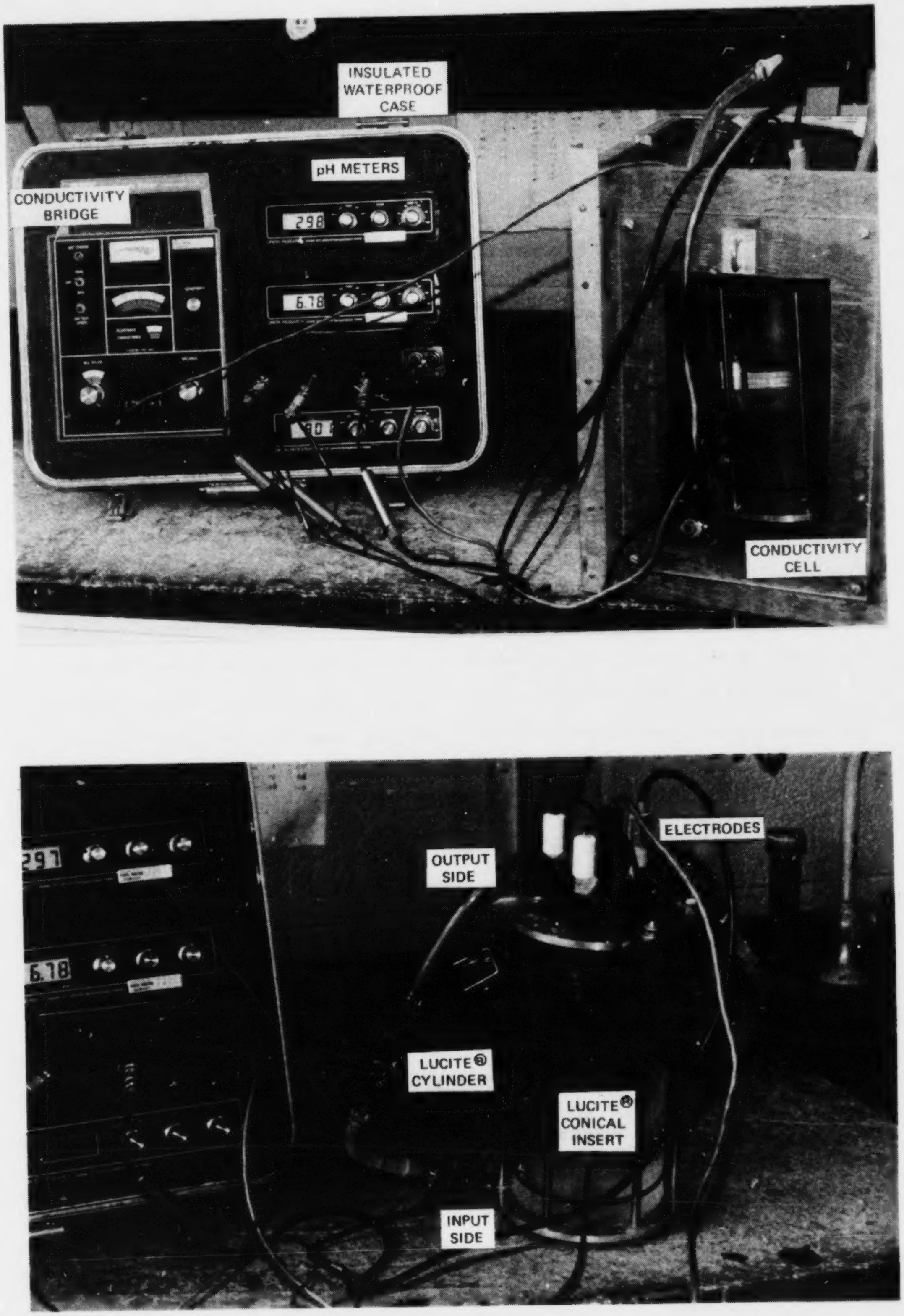
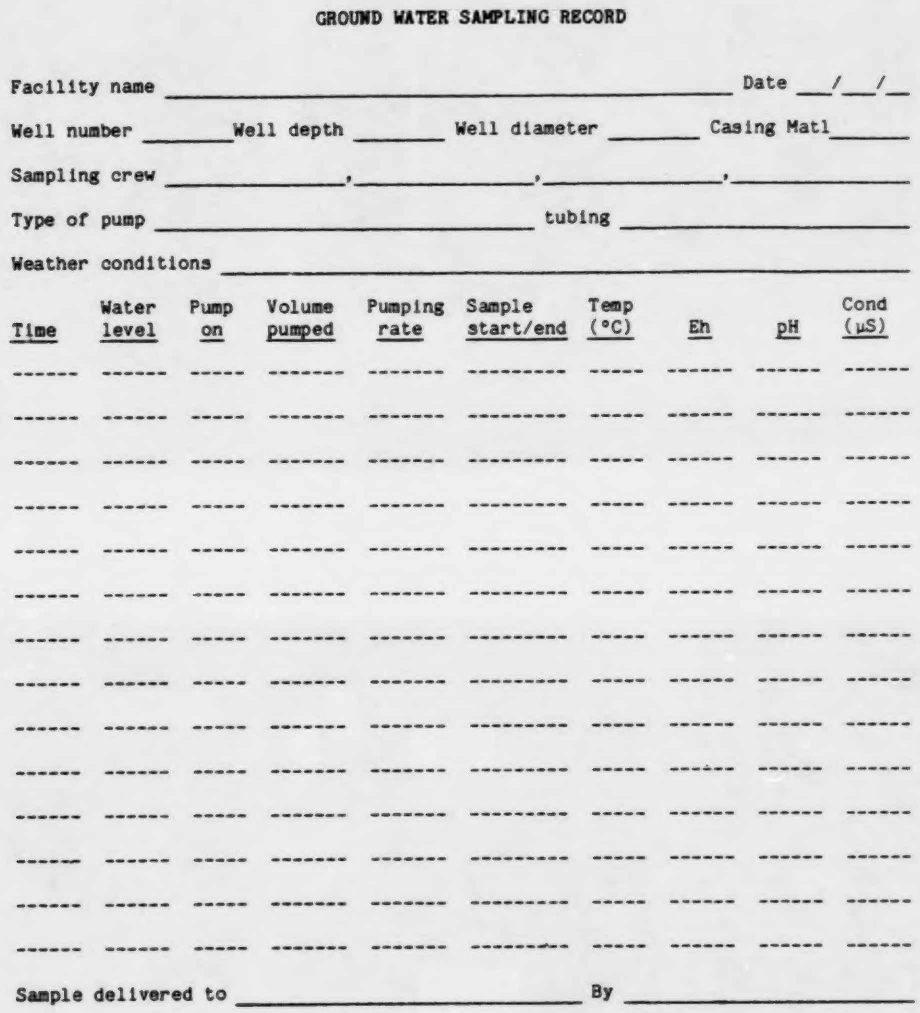

INSULATED WATERPROOF CASE
pH METERS
CONDUCTIVITY BRIDGE
2.98
6.78
CONDUCTIVITY CELL
2.97
6.78
ELECTRODES
OUTPUT SIDE
LUCITE® CYLINDER
LUCITE® CONICAL INSERT
INPUT SIDE

Figure 2.17. A well-head instrumentation package for Eh, pH, conductivity and temperature measurements



GROUND WATER SAMPLING RECORD

Facility name ______________________________ Date ___/___/___

Well number _______ Well depth _______ Well diameter _______ Casing Matl_______

Sampling crew _______________, _______________, _______________, _______________

Type of pump ______________________________ tubing _______________________

Weather conditions ____

Time	Water level	Pump on	Volume pumped	Pumping rate	Sample start/end	Temp (°C)	Eh	pH	Cond (µS)
------	------	-----	-------	-------	---------	-----	------	------	------
------	------	-----	-------	-------	---------	-----	------	------	------
------	------	-----	-------	-------	---------	-----	------	------	------
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Sample delivered to ___________________________ By _______________________

Figure 2.18. Suggested recording format for well purging and sample collection

notebook as that of the discrete samples for field or laboratory determinations. Regardless of the level of analytical detail in the monitoring program, it is essential that all samples be collected properly and that the actual conditions during each sample collection are completely documented. One member of the sampling staff should be designated as responsible for this documentation.

The format for documentation should be clear and constant during the overall program. A set of useful forms for field collection and measurement are presented in Tables 2.8 and 2.9. They are largely self-explanatory. It is useful to standardize the format, particularly where field personnel are responsible for splitting samples for field spikes or blind control samples. It is recommended to inscribe the bottles with an identifying marking which, when combined with the date of sampling, will uniquely identify it in a sampled set.

Water samples should be collected when the solution chemistry of the ground water being pumped has stabilized as indicated by pH, Eh, Ω^{-1} and T readings. In practice, stable sample chemistry is indicated when the purging parameter measurements have stabilized with ±10% over 2 successive well volumes. First, samples for volatile constituents, TOC, TOX and those constituents which require field filtration or field determination should be collected. Then large volume samples for extractible organic compounds, total metals or nutrient anion determinations should be collected.

All samples should be collected as close as possible to the well head. A "tee" fitting placed ahead of the in-line device for measuring the well purging parameters makes this more convenient. Regardless of

Table 2.8. Inorganic Sample Log (Filtered Samples)

Date 1/1/84 (time)	Well #	Alkalinity (Field) #	Alkalinity (Field) Volume (mL)	Major anions (HDPE) #	Major anions (HDPE) Volume (L)	Major cations (HDPE) #	Major cations (HDPE) Volume (L)	Trace metal ions (HDPE) #	Trace metal ions (HDPE) Volume
	1	1A	X		X		X		X
AM		1B							
PM		1C							
		1D							
	2	2A	X		X		X		X
AM		2B							
PM		2C							
		2D							
	3	3A	X		X		X		X
AM		3B							
PM		3C							
		3D							
	4	4A	X		X		X		X
AM		4B							
PM		4C							
		4D							
Field Blank			Conc. (ppm)	Conc. (ppm)		Conc. (ppm)		Conc. (ppb)	
		11B	0	0		0		0	
		12B	0	0		0		0	
Field Standard									
		11ST	100	25		50		100	
		12ST	250	50		100		250	
Split Sample Spike									
		4ASS	100	25		50		100	
		4ASS	200	50		100		200	

HDPE = Acid Rinsed, High Density Polyethylene Bottles, Preserved with 1 mL HNO_3/Liter
X = Filtered

Table 2.9. Organic Sample Log (Lab Filtered, If Necessary)

Date 1/1/84 (Time)	Well #	TOC		TOX		Volatiles		Extractables A		Extractables B (etc.)	
		(←-----------------40 mL amber glass vials				-------------------→)		(←----------TFE sealed		amber glass---------→)	
		#	Volume	#	Volume	#	Volume	#	Volume (L)	#	Volume (L)
	1	1AO									
AM		1BO									
PM		1CO									
		1DO									
	2	2AO									
AM		2BO									
PM		2CO									
		2DO									
	3	3AO									
AM		3BO									
PM		3CO									
		3DO									
	4	4AO									
AM		4BO									
PM		4CO									
		4DO									
Field Blank			Conc. (ppm)	Conc. (ppb)		Conc. (ppb)		Conc. (ppb)		Conc. (ppb)	
		11BO	0	0		0		0		0	
		12BO	0	0		0		0		0	
Field Standard											
		11STO	2	25		25		50		25	
		12STO	5	50		50		50		50	
Split Sample Spike											
		4AO-SS	2	25		25		25		25	
		4BO-SS	5	50		50		50		50	
Preservation			4°C/dark	4°C/dark		4°C/dark		←----------Refrigerate-----------→ 4°C			

the sampling mechanism in use or the components of the sampling train, upgradient wells should be sampled first followed by the downgradient wells to minimize the potential for cross-contamination. Laboratory detergent solutions and distilled water should be used to clean the sampling train between samples. An acid rinse (0.1 N HCl) or solvent rinse (i.e. hexane or methanol) should be used to supplement these cleaning steps if necessary. All cleaning should be followed by distilled water rinses which may be saved to check cleaning efficiency.

Adhesive labels or "indelible" markers can present sample identification problems, particularly when a variety of samples, split-samples, standards and blanks are transported in ice chests. The markings can be floated off or abraded into an illegible condition during transit.

Serious problems in sample handling and storage can result if extreme care is not taken during transport and storage. *All ice*, *ice packs*, and *ice-chests* should be prepared in areas that are remote from reagent and solvent storage of any kind! Further, the interim storage of these materials should also be remote from reagent or solvent storage areas. These precautions will minimize the effect of contamination errors on the results (79).

Filtration

There are instances which arise, even with properly developed monitoring wells, that call for the filtration of water samples. It should be evident, however, that well development procedures which require two to three hours of bailing, swabbing, pumping or air purging at each well will save many hours of time in sample filtration. Well development may have to be repeated at periodic intervals to minimize the collection of turbid samples. In this respect, it is important to minimize the disturbance of fines which accumulate in the well bore. This can be achieved by careful placement of the sampling pump intake at the top of the screened interval, low pumping rates, and by avoiding the use of bailers (60).

It is advisable to refrain from filtering TOC, TOX or other organic compound samples as the increased handling required may result in the loss of chemical constituents of interest. Allowing the samples to settle prior to analysis followed by decanting the sample is preferable to filtration in these instances. If filtration is necessary for the determination of extractable organic compounds, the filtration should be performed in the laboratory by the application of N_2 pressure. It may be necessary to run parallel sets of filtered and unfiltered samples with standards to establish the recovery of hydrophobic compounds when samples must be filered. All of the materials' precautions used in the construction of the sampling train should be observed for filtration apparatus. **Vacuum filtration of ground-water samples is not recommended.**

Water samples for dissolved inorganic chemical constituents (e.g. metals, alkalinity and anionic species) should be filtered in the field. The preferred arrangement is an in-line filtration module which utilizes sampling pump pressure for its operation. These modules have tubing connectors on the inlet and outlet parts and range in diameter from 2.5-15 cm. Large diameter filter holders, which can be rapidly dissembled for filter pad replacement are the most convenient and efficient designs (80,81).

The choice of filter media must be made on the basis of its exposure to the water samples and the degree of analytical detail required for those samples. Clearly, water samples which may be contaminated with organic solvents limit the use of organic filter media, such as cellulose nitrate, cellulose acetate or polycarbonate filters. In these cases glass fiber or Teflon$^{(R)}$ filter media should be used. Glass fiber filters should be acid rinsed followed by distilled water rinsed prior to their use for filtering trace metal or nutrient samples. Once an appropriate filter media has been selected, it is advisable to choose a 0.45 μM nominal sized filter. The final selection of the material and type of filter pad should be made carefully, as there are considerable differences between "screen" or "depth" filtration media (82). Screen filters are typically less than 50 μM thick (e.g. polycarbonate filters) which tend to load up and clog more rapidly than the depth-type filters. Sampling staff should be trained in proper procedures for filter pad replacement, since fine particles can easily be transferred to the outlet side of a dissembled filter module. Sloppy technique may result in solids breakthrough and biased samples. After a filter pad is charged, the initial 50-100 mL should be discarded as a rinse. Even if very careful procedures are followed, clogging and small particle breakthrough are real problems which must be addressed on a case by case basis (82,83).

Field Versus Laboratory Determinations

Representative sampling results from the execution of a carefully planned sampling protocol which establishes necessary hydrologic and chemical data for each sample collection effort. An important consideration for maintaining sample integrity, after collection, is to minimize sample handling which may bias subsequent determinations of chemical constituents. Since opportunities to collect high quality data for the characterization of site conditions in time may be limited, it is prudent to conduct sample collection as carefully as possible from the outset. It is preferable to bias data on the conservative side when doubt exists as to the sensitivity of specific chemical constituents to sampling or handling errors. Repeat sampling or analysis cannot make up for lost data collection opportunities.

Samples collected for specific chemical constituents may require modifications of recommended sample handling and analysis procedures. Matrix effects and extended storage periods can cause significant problems in this regard. It is frequently more effective to perform a rapid field determination of specific inorganic constituents (e.g. alkalinity, pH, ferrous iron, sulfide, nitrite or ammonium) than to attempt sample preservation followed by laboratory analysis of these samples. There are several good references to guide the development of field analytical procedures (1,2,31). Korte and Ealey (84) have prepared a useful field analytical guide. However, their recommendation not to filter alkalinity samples is not supported by the literature. Pressure filtration is necessary to insure that the alkalinity results are reliable for subsequent calculations of solution chemistry equilibria (85).

Criteria for the selection of appropriate analytical methods vary somewhat and the degree of analytical detail required for ground-water monitoring programs is increasing. It is advisable to select field and laboratory analytical methods carefully after consultation with the proper authorities. One should keep in mind that methods for drinking water or wastewater may encounter significant interferences when applied to contaminated ground-water samples.

Blanks, Standards and Quality Assurance

The use of field blanks, standards and spiked samples for field QA/QC performance is analogous to the use of laboratory blanks, standards and procedural or validation standards. The fundamental goal of field QC is to insure that the sampling protocol is being executed faithfully and that situations leading to error are recognized before they seriously impact the data. The use of field blanks and standards and spiked samples can account for changes in samples which occur after sample collection.

Field blanks and standards enable quantitative correction for bias (i.e., systematic errors), which arise due to handling, storage, transport and laboratory procedures. Spiked samples and blind controls provide the means to correct combined sampling and analytical accuracy or recoveries for the actual conditions to which the samples have been exposed. *All QC measures should be performed for at least the most sensitive chemical constituents for each sampling date.* Examples of sensitive constituents would be: benzene or trichloroethylene as volatile organic compounds and lead or iron as metals. It is difficult to use laboratory blanks alone for the determination of the limits of detection or quantitation. Laboratory distilled water may contain higher levels of volatile organic compounds (e.g. methylene chloride) than those of uncontaminated ground-water samples. The field blanks and spiked samples should be used for this purpose, conserving the results of lab blanks as checks on elevated laboratory background levels. The usefulness of spiked samples should be obvious. Whether the ground-water is contaminated with interfering compounds or not, these samples provide a basis for both the identification of the constituents of interest and the correction of their recovery (or accuracy) based on the recovery of the spiked standard compounds. For example, if trichloroethylene in a spiked sample is recovered at a mean level of 80% (-20% bias), the concentrations of trichloroethylene determined in the samples for this sampling date may be corrected by a factor of 1.2 for low recovery. Similarly, if 50% recovery (-50% bias) is reported for the spiked standard, it is likely that sample handling or analytical procedures are out of control and corrective measures should be taken at once. It is important to know if the laboratory has performed these corrections or taken corrective action when they report the results of analyses. It should be noted that many regulatory agencies require evidence of QC and analytical performance but do not generally accept data which has been corrected.

Field blanks, standards and blind control samples provide independent checks on handling and storage as well as the performance of the analytical laboratory. It should be noted that ground-water analytical data is incomplete unless the analytical performance data (e.g. accuracy, precision, detection, and quantitation limits) are reported along with each set of results. Discussions of whether significant changes in ground-water quality have indeed occurred must be tempered by the accuracy and precision performance for specific chemical constituents.

Table 2.10 is a useful guide to the preparation of field standards, and spiking solutions for split samples. It is important that the field blanks and standards be made on the day of sampling and are subjected to all conditions to which the samples are exposed. Field spiked samples or blind controls should be prepared in the field by spiking with concentrated stock standards in an appropriate background solution. The choice of spiking solution is particularly critical where volatile organic compounds are of concern (e.g. TOC, TOX and purgeables). In this case, pure poly(ethylene glycol) or water:poly(ethylene glycol) mixtures are very useful (86). The use of methylene chloride as a standard compound should be avoided. Additional precautions should be taken against the depressurization of samples during air transport and the effects of undue exposure to light during sample handling and storage. All of the QC measures noted above will provide both a basis for high quality data reporting and a known degree of confidence in data interpretation. Well planned quality control programs will also minimize the uncertainty in long-term trends when different personnel have been involved in sample collection and analysis.

Sample Storage and Transport

The storage and transport of ground-water samples are often the most neglected elements of the sampling protocol. Due care must taken in sample collection, field determinations and handling. If proper planning of transport is neglected the samples may be stored for long periods before laboratory analysis. Every effort should be made to

Table 2.10. Field Standard and Sample Spiking Solutions

Sample type	Volume	Composition	Field standard (concentration)	Stock solution for field spike of split samples		
				Solvent	Concentration of components	Field spike volume
Alkalinity	50 mL	Na^+, HCO_3^-	10.0; 250 (ppm)	H_2O	10,000; 25,000 (ppm)	(50 µL)
Anions	1 L	K^+, Na^+, Cl^-, $SO_4^=$	25, 50 (ppm)	H_2O	25,000; 50,000 (ppm)	(1 mL)
		F^-, NO_3^-, $PO_4^{\equiv}$, SI				
Cations	1 L	Na^+, K^+	5.0; 10.0 (ppm)	H_2O, H^+ (acid)	5,000; 10,000 (ppm)	(1 mL)
		Ca^{++}, Mg^{++}, Cl^-, NO_3^-				
Trace metals	1 L	Cd^{++}, Cu^{++}, Pb^{++}	10.0; 25.0 (ppm)	H_2O, H^+ (acid)	10,000; 25,000 (ppm)	(1 mL)
		Cr^{+++}, Ni^{2+}, Ag^+				
		Fe^{+++}, Mn^{++}				
TOC	40 mL	Acetone	0.2; 0.5 (ppm-C)	H_2O	200; 500 (ppm-C)	
		KHP	1.8; 4.5 (ppm-C)		1,800; 4,500 (ppm-C)	(40 µL)
TOX	40 mL	Chloroform	12.5; 25 (ppb)	H_2O/poly*	12,500; 25,000 (ppm)	
		2,4,6 Trichlorophenol	12.5; 25 (ppb)	(ethylene glycol)	12,500; 25,000 (ppm)	(40 µL)
Volatiles	40 mL	Dichlorobutane, Toluene		H_2O/poly*		
		Dibromopropane, Xylene	25; 50 (ppb)	(ethylene glycol)	25; 50 (ppm)	(40 µL)
Extractables A	1 L	Phenol Standards	25; 50 (ppb)	Methanol**	25; 50 (ppm)	(1 mL)
Extractables B	1 L	Polynuclear Aromatic Standards	25; 50 (ppb)	Methanol	25; 50 (ppm)	(1 mL)
Extractables C	1 L	Standards As Required	25; 50 (ppb)	Methanol	25; 50 (ppm)	(1 mL)

* - 75:25 Water/Polyethylene Glycol (400 amu) Mixture
** - Glass Distilled Methanol

inform the laboratory staff of the approximate time of arrival so that the most critical analytical determinations can be made within recommended storage periods. This may require that sampling schedules be adjusted so that the samples arrive at the laboratory during working hours.

The documentation of actual sample storage and treatment may be handled by the use of chain of custody procedures. An example of a chain of custody form is shown in Figure 2.19. Briefly, the chain of custody record should contain the dates and times of collection, receipt and completion of all the analyses on a particular set of samples. It frequently is the only record of the actual storage period prior to the reporting of analytical results that exists. The sampling staff members who initiate the chain of custody should require that a copy of the form be returned to them with the analytical report. Otherwise, verification of sample storage and handling will be incomplete.

Sample shipment arrangements should be planned to insure that samples are neither lost nor damaged enroute to the laboratory. There are several commercial suppliers of sampling kits which permit refrigeration by freezer packs and include proper packing. It may be useful to include special labels or distinctive storage vessels for acid-preserved samples to accommodate shipping restrictions.

CHAIN OF CUSTODY RECORD

Sampling Date ____________ Site Name ______________________________

Well or Sampling Points: ____

____

Sample Sets for Each: Inorganic, Organic, Both

Inclusive Sample Numbers:

Company's Name ___________________________ Telephone (___) ________

Address ____
number street city state zip

Collector's Name __________________________ Telephone (___) ________

Date Sampled __________ Time Started ______ Time Completed _________

Field Information (Precautions, Number of Samples, Number of Sample Boxes, Etc.):

1. ____
name organization location
2. ____
name organization location

Chain of Possession (After samples are transported off-site or to laboratory):

1. ____________________ _____________________ _____ ____ (IN)
signature title
____________________ _____________________ _____ ____(OUT)
name (printed) date/time of receipt
2. ____________________ _____________________ _____ ____ (IN)
signature title
____________________ _____________________ _____ ____(OUT)
name (printed) date/time of receipt

Analysis Information:

	Aliquot	Analysis Begun (date/time)	Initials	Analysis Completed (date/time)	Initials
1.					
2.					
3.					
4.					
5.					

Figure 2.19. Sample chain of custody form

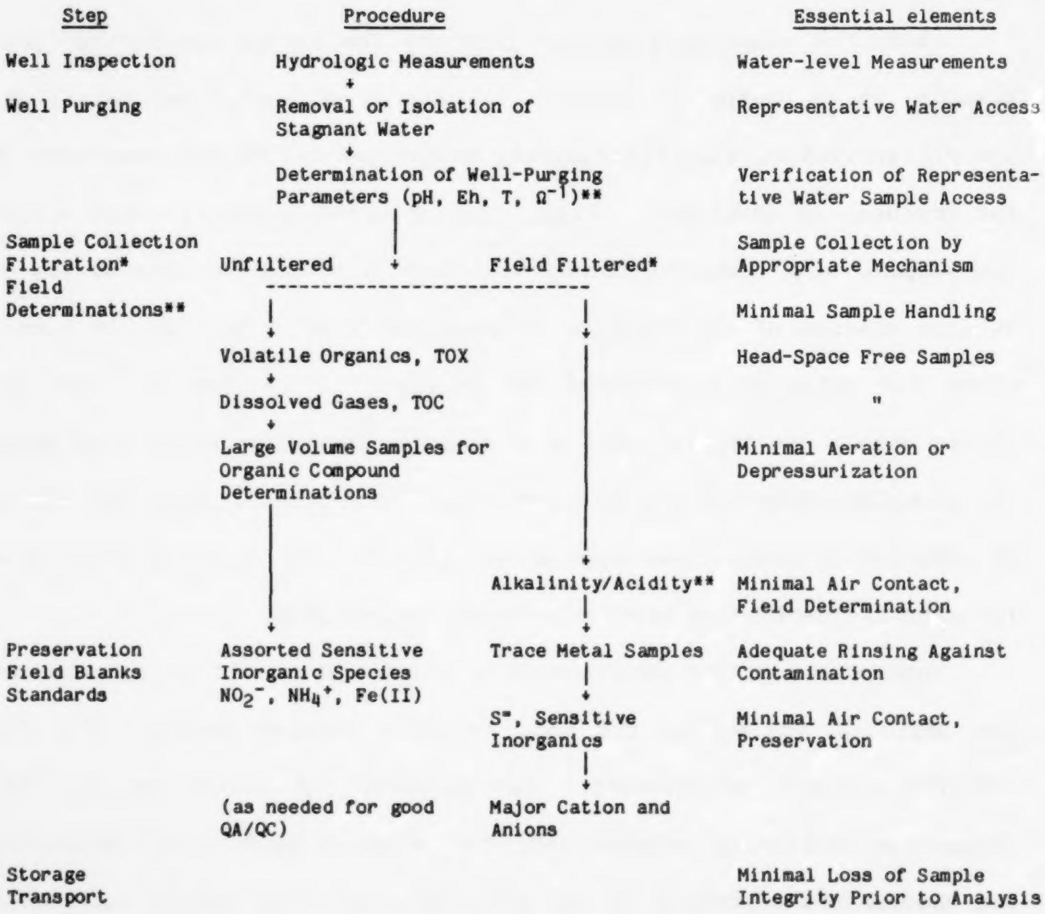
SECTION 3
RECOMMENDED SAMPLING PROTOCOLS

The selection of methods and materials for drilling and well construction, sampling and sample handling should be based on a complete evaluation of site conditions, the analytes of interest and the information needs of the program. Integrating all of these elements into a reliable sampling protocol must be done in phases as information on the actual conditions at a site is collected. Sampling mechanisms and materials are central to effective monitoring efforts. However, mechanisms and materials' selections are only the basis for the development of the sampling protocol. The preliminary protocol must be documented and all personnel involved in the effort should be well acquainted with it. Then the sampling protocol can be refined and targeted in development to meet the critical information needs of the overall program.

In this section, specific recommendations are made for preliminary sampling protocols applicable to both contaminant detection and assessment programs. General guidelines are presented with a step by step description of the procedures to develop of specific sampling protocols for a variety of monitoring applications.

THE BASIS FOR SAMPLING PROTOCOL DEVELOPMENT

The individual elements of effective sampling protocols have been reviewed in Section 2 of this guide. The generalized sampling protocol presented in Figure 2.16 provides a review of the procedures undertaken at each step. Figure 3.1 provides a prioritized schematic for the execution of steps within the overall protocol which should guide the



Step	Procedure		Essential elements
Well Inspection	Hydrologic Measurements		Water-level Measurements
Well Purging	Removal or Isolation of Stagnant Water		Representative Water Access
	Determination of Well-Purging Parameters (pH, Eh, T, Ω^{-1})**		Verification of Representative Water Sample Access
Sample Collection Filtration* Field Determinations**	Unfiltered	Field Filtered*	Sample Collection by Appropriate Mechanism
			Minimal Sample Handling
	Volatile Organics, TOX		Head-Space Free Samples
	Dissolved Gases, TOC		"
	Large Volume Samples for Organic Compound Determinations		Minimal Aeration or Depressurization
		Alkalinity/Acidity**	Minimal Air Contact, Field Determination
Preservation Field Blanks Standards	Assorted Sensitive Inorganic Species NO_2^-, NH_4^+, Fe(II)	Trace Metal Samples	Adequate Rinsing Against Contamination
		$S^=$, Sensitive Inorganics	Minimal Air Contact, Preservation
	(as needed for good QA/QC)	Major Cation and Anions	
Storage Transport			Minimal Loss of Sample Integrity Prior to Analysis

*Denotes samples which should be filtered in order to determine dissolved constituents. Filtration should be accomplished preferably with in-line filters and pump pressure or by N_2 pressure methods. Samples for dissolved gases or volatile organics should not be filtered. In instances where well development procedures do not allow for turbidity-free samples and may bias analytical results, split samples should be spiked with standards before filtration. Both spiked samples and regular samples should be analyzed to determine recoveries from both types of handling.

**Denotes analytical determinations which should be made in the field.

Figure 3.1. Generalized flow diagram of ground-water sampling steps

planning of sampling efforts. Essential considerations for the reliability of each step are also provided in the figure to aid planning specific efforts. The planning should be coordinated with supervisory, field, and laboratory staff.

Since the sampling mechanism provides the sample for further processing, it is useful to consider the degree of analytical detail and the reliability of specific sampling mechanisms before the remainder of the protocol is developed. Figure 3.2 provides a matrix which allows the comparison of sampling mechanism reliability with the sensitivity of various classes of constituents to sampling error. This matrix summarizes the detailed recommendations provided in Section 2. Its use should enable the initial choice of sampling mechanism which will serve the planning needs for a preliminary sampling protocol. Once the choice of sampling mechanism has been made, step-by-step sampling procedures for specific monitoring applications may be designed.

Appropriate ground-water sampling procedures should be selected on the basis of collecting the most reliable samples possible for the specific analytes of interest. For purposes of discussion, one may categorize monitoring efforts into two broad classes (i.e., detection and assessment) according to the level of analytical detail sufficient for the information needs of the program.

SAMPLING PROTOCOLS FOR DETECTION MONITORING

In detection monitoring efforts, the information needs are mainly to detect ground-water contamination and to establish a set of useful ground-water quality data in the event that contamination is detected.

Type of constituent	Example of constituent		Positive displacement bladder pumps	Thief, in situ or dual check valve bailers	Mechanical positive displacement pumps	Gas-Drive devices	Suction mechanisms
			←-------------------------- INCREASING RELIABILITY OF SAMPLING MECHANISMS				
Volatile Organic Compounds Organometallics	Chloroform TOX CH_3Hg	INCREAS	Superior Performance	May be adequate if well purging is assured	May be adequate if design and operation are controlled	Not recommended	Not recommended
Dissolved Gases Well-Purging Parameters	O_2, CO_2 pH, Ω^{-1} Eh	ING SAM	for	May be adequate if well purging is assured	May be adequate if design and operation are controlled	Not recommended	Not recommended
Trace Inorganic Metal Species Reduced Species	Fe, Cu NO_2^-, $S^=$	PLE SENS	most	May be adequate if well purging is assured	Adequate	May be adequate	May be adequate if materials are appropriate
Major Cations & Anions	Na^+, K^+, Ca^{++} Mg^{++} Cl^-, $SO_4^=$	ITIVITY	Applications	Adequate May be adequate if well purging is assured	Adequate	Adequate	Adequate

Figure 3.2. Matrix of sensitive chemical constituents and various sampling mechanisms

Analyte Selection and Sampling Recommendations

A list of the corresponding regulated parameters for a detective monitoring effort is provided in Table 3.1. The listing includes parameters of the following types: well purging, contamination indicator, water quality and those that establish drinking water suitability. The well-purging parameters provide both a measure of the efficiency of the well-evacuation procedures prior to the collection of samples and valuable data (e.g. Eh, pH, Ω^{-1}, T) for the evaluation or interpretation of water chemistry results. The contamination indicator parameters (e.g. pH, Ω^{-1}, TOC, TOX) may indicate whether or not gross changes in ground-water solution composition have occurred due to a contaminant release. The sensitivity of these indicator parameters is somewhat limited with the exception of TOX which can be determined reliably at sub-ppm ($\mu g \cdot L^{-1}$) levels.

Water quality parameters provide useful information for description of the ground-water system, particularly when the regulated constituents (e.g. Cl^-, Fe, Mn, Na^+, $SO_4^=$ and phenols) are supplemented with the major cations and ions which usually comprise the bulk of the dissolved solids in natural water samples. The water quality parameters may be used as a basis for comparison in the event that the monitoring program is triggered into an assessment phase. More importantly, the characterization of the inorganic chemical composition of ground water enables both the quantitative interpretation of the consistency of the analytical results and the potential to calculate the chemical speciation of specific dissolved chemical constituents. It is the speciation of chemical constituents which enables the prediction of their reactivity,

Table 3.1. Recommended Analytical Parameters for Detective Monitoring

Type of parameter	Type of determination Lab. (L), Field (F)	Analytes: Required by regulation	Analytes: Suggested for completeness
Well-purging	F	pH, conductivity (Ω^{-1})	Temperature (T) Redox potential (Eh)
Contamination indicators	F	pH, Ω^{-1}	
	L	Total organic carbon (TOC)	
	L	Total organic halogen (TOX)	
Water quality	L	Cl^-, Fe, Mn, Na^+, $SO_4^=$	Alkalinity (F) or acidity (F)
	L	Phenols	Ca^{++}, Mg^{++}, K^+, NO_3^-, $PO_4^{\equiv}$, silicate, ammonium
Drinking water suitability**	L	As, Ba,Cd, Cr, F^-, Pb, Hg, NO_3^-, Se, Ag	
	L	Endrin, lindane, methoxychlor, toxaphene 2,4-D, 2,4,5-TP (Silvex)	
	L	Radium, gross alpha/beta coliform bacteria	

* All parameters are required to be determined quarterly for the first year of network operation. RCRA Part 265.92.

** These parameters are excluded from the annual reporting requirements of RCRA after the first year.

solubility and mobility under the actual conditions at the site. [It should be noted that mass and charge balance consistency of the analytical results is a pre-condition for the reliable application of equilibrium speciation models.] The drinking water suitability parameters are often required to be determined in the first year of network operation on a quarterly basis by monitoring regulations. They may be excluded from annual reporting requirement in succeeding years. One year of quarterly data for these parameters may not be sufficient, since potable water wells may often be used as background (upgradient) components of a monitoring network if the original upgradient wells of the network prove to be contaminated. These requirements may vary somewhat based on current monitoring regulations. Field blanks, standards and spiked samples should be done at the same degree of replication for all parameters on each sampling date.

In summary, recommended parameters for detective monitoring programs provide a minimum capability to detect contamination and to serve as a basis for comparison and planning, should the program enter the assessment phase. Depending on the hydrologic conditions at the site, higher sampling frequency (e.g. monthly) will provide a better set of baseline data for future trend analysis or upgradient-downgradient comparisons.

Many ground-water monitoring programs will entail the determination of the sensitive chemical parameters noted in Table 3.1. These parameters demand the careful selection of both field and laboratory sample handling (e.g. pumping, transfer, collection and storage) and analytical procedures. For example, levels of pH, Eh, TOC, TOX, alkalinity, ammonium, Fe and other trace metals are prone to serious bias (i.e. loss or inaccuracy) and imprecision (i.e. inconsistent duplicates, high analytical variance) if volatilization, aeration or degassing occurs during sample handling or analysis. The severity of these problems will be a function of solution composition, field conditions and the complexity of the actual procedures employed. It should be recognized that the simplest procedures which minimize sample handling and exposure to the atmosphere or agitation will provide the most reliable results. Therefore, the use of a sampling mechanism which provides flow sufficient for well purging and a *steady stream* of ground-water for the in-line determination of well-purging parameters (and in-line filtration)is preferred. This type of mechanism will enable the *controlled transfer* and *collection* of discrete samples for both field and laboratory determinations of specific chemical parameters. Where ground-water availability is a problem, discrete samples must be collected with every effort to preserve sample integrity. A schematic diagram of recommended sample collection, and handling methods for detection monitoring programs, is shown in Figure 3.3. Specifics on sample handling and preservation are provided in Table 3.2. These recommendations have been based on the available information from the literature.

ASSESSMENT MONITORING

The information needs of assessment monitoring efforts are more detailed than those involved in detection monitoring. In detection monitoring, the indication of contamination and the establishment of a basis for ground-water quality comparisons are the principal goals. In the assessment phase, the nature, extent and dynamics of a contaminated

Parameters	Mechanism	Hydrogeologic Conditions (yield capability)	
(type)	(material)*	>100 mL/min yield	<100 mL/min yield
		Flowing samples	Discrete samples
Well-purging (pH, Eh, T, Ω^{-1})	Pump (T,S,P,O) Flow rates: 0.1-1.0 L/min	Positive displacement bladder pump (air, N_2)	
	Grab (T,S,G,P,O)		Dual check valve bailers "thief" samplers
Contamination Indicators (pH, Ω^{-1})	Pump (T,S,P,O) Flow rates: 0.1-1.0 L/min	Positive displacement bladder pump (air, N_2)	
	Grab (T,S,G,P,O)		Dual check valve bailers "thief" samplers
(TOC, TOX)	Pump (T,S preferred; O,P only where supporting data exists)	(Mechanisms as above operated at flow rates not to exceed 100 mL/min) 40 mL vials filled gently from bottom up and allowed to overflow → Teflon capped w/o headspace	(Volatile fractions of TOC and TOX may be lost depending on conditions and operator skill)
	Grab (T,S,G preferred; O,P only where supporting data exists)		40 mL vials filled from bottom up and allowed to overflow or gently poured down the side of the vial, Teflon capped w/o headspace

* Materials in order of preference include: Teflon (T); stainless steel (S); PVC, polypropylene, polyethylene (P); borosilicate glass (G); other materials: silicone, polycarbonate, mild steel, etc. (O)

(continued on next page)

Figure 3.3 Recommended sample collection methods for detective monitoring programs

Parameters (type)	Mechanism (material)*	Hydrogeologic Conditions (yield capability)	
		>100 mL/min yield	<100 mL/min yield
		Flowing samples	Discrete samples
Water Quality Dissolved Gases (O_2, CH_4, CO_2)	Pump (T,S,P,O)	(Mechanisms as above operated at flow rates not to exceed 100 mL/min) Glass containers filled gently from bottom up and allowed to overflow → Teflon capped w/o headspace	(Not recommended)
Alky/Acdy	Grab (T,S,G,P,O)		
(Fe, Mn, $PO_4^{\equiv}$, Cl^-, Na^+, $SO_4^=$, Ca^{++}, Mg^{++}, K^+, NO_3^-, Silicate)	Pump (T,S,P,O) Grab (T,S,G,P,O)	Positive displacement bladder pump (air, N_2)	Fe values sensitive to most grab mechanisms Large volumes required may have to be sequentially collected and filtered
(Ammonium, Phenols)	Pump (T,S preferred; O,P only where supporting data exists) Grab (T,S,G preferred; O,P only where supporting data exists)	(Mechanisms as above operated at flow rates not to exceed 1000 mL/min) Glass containers filled from bottom up	(Volatile species may be lost depending on conditions) Glass containers filled from bottom up

* Materials in order of preference include: Teflon (T); stainless steel (S); PVC, polypropylene, polyethylene (P); borosilicate glass (G); other materials: silicone, polycarbonate, mild steel, etc. (O)

(concluded on next page)

Figure 3.3. (continued)

Parameters	Mechanism	Hydrogeologic Conditions (yield capability)	
		>100 mL/min yield	<100 mL/min yield
(type)	(material)*	Flowing samples	Discrete samples
Drinking Water Suitability	Pump (T,S,P,O)	Positive displacement bladder pump (air, N_2)	
(As, Ba, Cd, Cr, Pb, Hg, Se, Ag, NO_3^-, F^-)	Grab (T,S,G,P,O)		Dual check valve bailers "thief" samplers
(Remaining Parameters)	Pump (T,S,P,O)	Positive displacement bladder pump (air, N_2)	(Volatile compounds may be lost depending on conditions)
	Grab (T,S,G,P,O)	Flow rates should not exceed 1,000 mL/min	
	(both with precautions if radiologic hazards exist)		

* Materials in order of preference include: Teflon (T); stainless steel (S); PVC, polypropylene, polyethylene (P); borosilicate glass (G); other materials: silicone, polycarbonate, mild steel, etc. (O)

Figure 3.3. (concluded)

Table 3.2. Recommended Sample Handling and Preservation Procedures for a Detective Monitoring Program*

Parameters (type)	Volume required 1 sample**	Container (material)	Preservation method	Maximum holding period
Well purging				
pH (grab)	50	T,S,P,G	None-Field Det.	<1 hr.***
Ω^{-1} (grab)	100	T,S,P,B	None-Field Det.	<1 hr.***
T (grab)	1000	T,S,P,G	None-Field Det.	None
Eh (grab)	1000	T,S,P,G	None-Field Det.	None
Contamination indicators				
pH, Ω^{-1} (grab)	As above	As above	As above	As above
TOC	40	G,T	Dark, 4°C	24 hrs.
TOX	100	G,T	Dark, 4°C	5 days
Water quality				
Dissolved gases (O_2, CH_4, CO_2)	10 mL minimum	G,S	Dark, 4°C	<24 hrs.
Alkalinity/ Acidity	100	T,G,P	4°C/None	<6 hrs.***/<24 hrs.
	Filtered under pressure with appropriate media			
(Fe, Mn, Na^+, K^+, Ca^{++}, Mg^{++})	All filtered 1000 mL	T,P	Field acidified to pH <2 with HNO_3	6 months$^{\Delta}$
($PO_4^{\equiv}$, Cl^-, Silicate)	@ 50	(T,P,G glass only)	4°C	24 hrs./7 days; 7 days
NO_3^-	100	T,P,G	4°C	24 hrs.
$SO_4^=$	50	T,P,G	4°C	7 days
NH_4^+	400	T,P,G	4°C/H_2SO_4 to pH <2	24 hrs./7 days
Phenols	500	T,G	4°C/H_3PO_4 to pH <4	24 hrs.
Drinking water suitability				
As,Ba,Cd,Cr, Pb,Hg,Se,Ag	Same as above for water quality cations (Fe,Mn,etc.)	Same as above	Same as above	6 months
F^-	Same as chloride above	Same as above	Same as above	7 days
Remaining organic parameters	As for TOX/TOC, except where analytical method calls for acidification of sample			24 hrs.

* Modified after Scalf et al. (3)

** It is assumed that at each site, for each sampling date, replicates, a field blank and standards must be taken at equal volume to those of the samples.

*** Temperature correction must be made for reliable reporting. Variations greater than ±10% may result from longer holding period.

Δ In the event that HNO_3 cannot be used because of shipping restriction, the sample should be refrigerated to 4°C, shipped immediately, and acidified on receipt at the laboratory. Container should be rinsed with 1:1 HNO_3 and included with sample.

ground-water situation must be characterized sufficiently to plan further investigative or remedial action activities. The level of detail required in assessment efforts may be an order of magnitude more complex than those in the detective phase. Therefore, the reliability of the data in space and time must increase proportionately. Incomplete characterization of a ground-water sample's solution composition could lead to the incorrect assessment of the mobility or reactivity of potential contaminants. The three-dimensional extent of a contaminant pulse or plume might be lost if the bias introduced into the determination of the principal contaminants is high relative to background concentrations. Remedial action or mitigative action decisions should be based on a high quality data set which meets the information needs of the program. Clearly the experience that operators gain during the detection phase of monitoring will prepare them for reliable assessment activities.

The well-purging and contamination indicator parameters are generally less sensitive to gross sampling and analytical errors than chemical constituents which may be specific components of a waste from a landfill, impoundment, waste-pile, spill or storage area. Predictions of the major contaminants involved and the subset of stable, mobile constituents that may be expected to be found downgradient must be made.

For example,assume that a well-executed detection monitoring effort at a solvent waste transport station disclosed that TOX values downgradient are significantly different from those collected during the past three quarters at upgradient wells. The mean upgradient value differs from that downgradient by 100 ppb which is of the order of five times the mean precision of the TOX determinations at these levels. The TOC data, on the other hand, show no statistically significant difference between the upgradient and downgradient wells. Since the precision of the TOC values are ±0.1 $mg \cdot L^{-1}$ at best, it is quite possible that the present contamination is the result of halogenated solvent releases. In this case it may be that hydrocarbon solvents or petroleum derived compounds are the likely constituents of interest in the assessment phase.

Reliable sampling of the TOX in the ground-water at the site may permit the scope of the initial assessment to be limited to halogenated compounds. Additional data would be helpful if the analytical results clearly reported both volatile and nonvolatile TOC and TOX. If, in the example above, the observed TOX increase was represented in a proportional increase only in the volatile TOX, the purgable organic compounds should be investigated in the initial assessment activity.

If the detective monitoring results disclose only secondary, nonvolatile contaminants (because the volatile fractions of TOC or TOX were lost during sample collection, handling or analysis), the consequences of relying on a poorly designed sampling protocol could be far more serious. Precision and bias for determinations of the detective monitoring parameters can be controlled in the ±10 to 50% range. However, order of magnitude levels of variance or loss may enter into sampling and analytical results for trace constituents at the ppb ($\mu g \cdot L^{-1}$) level. Poor precision and accuracy directly reduce the power of statistical tests for cxomparison of background and potentially affected downgradient conditions.

As the information needs of a monitoring program become more detailed it is essential to establish control over errors. Sample collection and handling problems for TOC and TOX which do not introduce additional bias or imprecision above those of the analytical methods may be expected to perform adequately for specific inorganic or organic chemical constituents of a contaminant release. This will be true if the chemical constituents of the product/waste release are known and their mobility or reactivity in the subsurface can be reasonably predicted. The actual selection of "facility-specific" constituents also may be very difficult to make if ground-water quality has not been well characterized in the detection monitoring phase.

Given the wide range of potential contaminants (e.g. potentially thousands of waste components in RCRA, Appendix VIII, etc. listings) and those which may be sensitive to sample collection or handling errors, it is difficult to make a priori evaluations of the adequacy of monitoring procedures or protocols. However, it is clear that proven sampling and sample handling procedures which control bias and precision at comparable levels of analytical method performance are most reliable. In this respect, Fe, pH, TOX and TOC results are parameters which may be used to gauge the utility of sampling protocols used in detection monitoring for application in contamination assessment work. One may generalize reliable sample collection and handling protocols on this basis.

Dissolved iron may be accepted as being representative of inorganic metallic species which are prone to oxidation and the formation of solid oxide or oxyhydroxide products. The oxide products have very active surfaces for the sorption of other metallic ions or organic compounds.

If water samples are not carefully collected (i.e. to exclude O_2 or gas exchange), handled (i.e. filtered under N_2 or pump presure prior to acidification), the reduced iron in many samples would oxidize prior to preservation and this reaction, as well as the inevitable sorptive interactions, could seriously bias the analytically determined composition of the ground water (87). By analogy, the target chemical constituents in an assessment program for metallic contamination (e.g. Cu, Cr, Ni from an acidic alloy treating process waste) should be sampled and handled reliably using the same procedures which permit reliable dissolved iron samples to be taken. It should be noted that although many RCRA Appendix VIII parameters are metallic and may require only metal determinations in the lab, the actual elemented speciation will impact the reliability of sampling procedures. This may be illustrated by inspection of Table 3.3. Analysis procedures should be streamlined to facilitate screening of water samples since the speciation of the metal may impact on sample preparations and all the steps which precede them (i.e. sample collection, transfer, filtration, preservation and storage). It is difficult to specify the optimum sampling procedures for water samples potentially contaminated with a variety of uncharacterized waste mixtures. However, a sampling protocol which is proven reliable for difficult or sensitive chemical constituents should perform adequately for most other parameters. Figure 3.2 contains a matrix of chemical constituents and appropriate sampling mechanisms. An increase in the degree of sampling difficulty or sensitivity to bias of a constituent requires that a more robust, fool-proof sampling mechanism be used. If alternative sampling methods are utilized which are not well

Table 3.3. Equipment for Field Sampling

Quantity	Item
1	Compressed N_2 cylinder (301 ft^3) for bladder pump sampling oxidation sensitive constituents if needed
2	Scuba tanks (compressed air) (80 ft^3 + 50 ft^3) for bladder pump
1	Alkalinity box (battery operated pH meter with temperature compensation, electrode, battery operated magnetic stirrer, buret, titrant, beakers)
1	Flow through cell in box with 3-way valve system to route pump output to cell (e.g. pH, 2 redox, temp. electrodes + conductivity cell) or to sample/waste (ref. Figure 2.18)
1	Meter box (3- pH meters (as above) + 1 battery operated temperature compensated conductivity bridge) (ref. Figure 2.18)
2	Regulators for gas cylinder + scuba tanks
3	Buckets (15 L) and graduated cylinder (5 L) to measure purge volume and sample waste
1	Dissolved oxygen field kit (Modified Winkler Method (46) 200 mL titration volume)
2	5 gallon (LDPE) water jugs for deionized water
2	Sampling pumps (primary plus a backup and an extra bladder assembly) Teflon/Teflon bladder and Stainless Steel/Teflon bladder
2	Pump tubing sets (Teflon) (1 air, 1 water, @ 50' + tubing holder, primary plus backup). Tubing diameter should be no less than 1/4" o.d. and the larger diameter sizes will minimize tubing material effects if they are anticipated)
1	Pump control box with tubing
1	Gas manifold (to operate multiple pumps from same compressed gas supply)
1	Steel measuring tape
1	Grass whip
1	Shovel

(concluded on next page)

Table 3.3. (concluded)

Quantity	Item
1	Miscellaneous box with (6 boxes Kimwipes, 3 boxes disposable gloves, aluminum foil, duct tape)
1	Miscellaneous box with (pH buffers, deionized wash bottle, Erlenmeyer flasks, beakers, graduate cylinders, pasteur pipettes, bulbs, conc. HNO_3 acid, conc. HCl acid, filter membranes, filter holders)
3	Shock cords
4	Coolers (insulated, 64 qt., 54 qt, 44 qt - one each)
3	Toolboxes

* Sample bottles for samples, spiked samples and extras

** Prepared bottles for field blanks and standards with spiking solutions

*** Sampling log, field notebooks, chain of custody forms referenced, supporting accuracy and precision data should be provided for the specific constituents of interest. Regardless of the sampling mechanism used, the elements of the generalized sampling protocol should be documented completely.

Field Sampling Procedures

This section of the guide is presented as an example of "how-to" collect samples as drawn from the authors' experiences. Refinement and modification will be necessary for application to specific sampling and analytical needs. In large measure, the degree of preparedness and skill which these individuals take into the field will determine the actual number of samples which can be collected. A well prepared team of three individuals can usually sample between 4-6 monitoring wells (0-75 ft. deep) in a full 8-hour day, exclusive of travel time. Given the range of field or hydrogeologic conditions, network complexities and the analytical detail which ground-water monitoring investigations demand, no single example can provide all of the elements needed in the sampling protocol. The following discussion should provide the basis for the application of effective sampling procedures for either detection or assessment monitoring investigations.

The following steps in a sampling protocol are covered in detail below:

Sampling Equipment Setup, Well Inspection and
Water Level Measurement

Verification of Well Purging Requirements

Sample Collection/Filtration/Field Blanks and Standards

Field Determinations

Sample Storage/Transport

The importance of careful integration of the efforts of sampling staff at each point should not be underestimated. Mistakes, lost data or biased results may exact a heavy price if sampling efforts are not well planned. The same care taken in the laboratory to prevent mishaps or contamination should be followed in the field. It should be obvious that smoking or eating in the vicinity of the well head, pump output or field analytical setups is strongly discouraged.

Sampling Equipment Setup, Well Inspection and Water Level Measurement

It is a good practice to have a detailed list of all sampling materials and supplies. The list should be reviewed before the sampling staff leaves for the field site. This somewhat tedious procedure will cut down on the frustration or anxiety which may arise later because of missing equipment, reagents or bottles. An example of a sampling equipment list is shown in Table 3.4 which includes the basic gear needed to conduct routine sampling and field activities. The list is reasonably complete for a protocol based on the use of a positive displacement bladder pump which is sufficient for the well-purging and sample collection requirements of many monitoring situations.

On arrival at the well-head, the condition of the surface seal and well protector should be examined to see if any evidence of frost-heaving, cracks or vandalism are observed, they should be recorded in the field notebook. The area around the well may have to be cleared of weeds or other materials prior to beginning the sampling activity. A drop cloth should then be placed on the ground around the well head,

Table 3.4. Metallic Species in RCRA Appendix VIII Which Require Only Metal Determinations

- * Antimony NOS
- Arsenic acid
- * Arsenic and compounds, NOS
- Arsenic pentoxide
- Arsenic trioxide
- * Barium and compounds, NOS
- Barium cyanide
- * Benzenearsonic acid
- * Beryllium and compounds, NOS
- * Cadmium and compounds, NOS
- Calcium chromate
- * Chromium and compounds, NOS
- Copper cyanide
- * Dichlorophenylarsine
- * Diethylarsine
- * Hydroxydimethylarsine oxide
- Lead acetate
- * Lead and compounds, NOS
- Lead phosphate
- Lead subacetate
- * Tetraethyl lead
- * Mercury and compounds, NOS
- * Mercury fulminate
- * Nickel and compounds, NOS
- * Nickel carbonyl
- Nickel cyanide
- Osmium tetroxide
- * Phenylmercury acetate
- Potassium silver cyanide
- * Selenium and compounds, NOS
- Selenious acid
- Selenium sulfide
- * Selenourea
- * Silver and compounds, NOS
- Silver cyanide
- Strontium sulfide
- Thallic oxide
- Thallium acetate
- * Thallium and compounds, NOS
- Thallium carbonate
- Thallium chloride
- Thallium nitrate
- Thallium selenite
- Thallium sulfate
- Vanadic acid, ammonium salt
- Vanadium pentoxide
- Zinc cyanide

NOS: Not otherwise specified; signifies those members of the general class not specifically listed by name in Appendix VIII.

* Metallic species which may exhibit markedly different properties (e.g. solubility, volatility, reactivity) from inorganic ions or complexes in ground water

particularly if the land surface is disturbed or potentially contaminated. This precaution will save time and the work of cleaning equipment or tubing should they fall on the ground during preparation or operation. The well protector should then be unlocked and the cap removed from the top of the well. The previous record of water levels for the well should be consulted prior to chalking the steel tape and making three successive measurements of the static water level. The readings should be recorded to the nearest ±0.01 ft. If the well has a history of contamination, the water level measurements should be made with surgical gloves on and the tape should be rinsed with distilled water and wiped dry with lint-free towels as it is wound on the reel. While the water level is being measured, the other sampling personnel should prepare to set up the pumping and flow-through measurement equipment and the instrumentation for analytical field determinations. Blanks and standards should be titrated for alkalinity and dissolved oxygen determinations at this time. Also, the pH meters, Eh electrode combinations and the conductivity bridge should be calibrated (78). The assembly of the Teflon and stainless steel bladder pump and the tubing bundles should be performed as well. Gloves should be worn at all times during pump assembly. These activities should take approximately 35-45 minutes and may be completed at a location central to all the wells which will be sampled during the day. At this point, the sample bottles should be checked for proper labelling. Then the field and sampling logs should be readied for the next steps. It is important to record the stagnant water volume in the well from the water level reading and compare it to that calculated for the well from the evaluation of pumping requirements.

Verification of the Well Purging Requirement

Well purging requirements should be calculated from the hydraulic performance of the well and verified each day by measurement of the well-purging parameters. Let us presume that the example well has been properly evaluated as to its hydraulic performance by the methods described in the examples in Section 2. In this case, the calculated purging requiement is approximately 80 L (~4 well volumes) which should be purged prior to the collection of representative samples. Since the well was developed at a flow rate of approximately 6 L/min, a conservative pumping rate of 3 L/min has been chosen for purging the well pumping rate of 1 L/min has been chosen. The pump is lowered to the point where the pump intake is at the top of the screened interval. It is useful to use a "keeper" which consists of a wooden or plastic rectangle with holes drilled in it to allow the gas and water tubes to slide through and be held in place with a knotted cord or wire tie. At this time the pump should be started and adjusted to produce a steady output through the flow-through cell and into a collection bucket or drum. At intervals equal to (10% of the calculated purging requirement (~8 L), the readings of Eh, pH, T, and Ω^{-1} are then recorded and the cumulative volume pumped (including that in the cell) should be measured and recorded. When the calculated purge volume is approached the readings should be made at more frequent volume intervals and the pump may be slowed to ~1,000 mL/min. When the readings of the well purging parameters have stabilized to within ±10% over two successive volume increments (i.e., no less than 20% of the required purge volume; ~16 L), the pump output may be considered equilibrated and sampling may begin. The data in Table 3.5 show the gradual stabilization of the pH and Ω^{-1} values at ~49 L which was verified by pumping through 16 more liters. In this example, about 80% of the calculated well purging requirement was pumped prior to equilibration.

Sample Collection/Filtration

Samples should be taken in a prearranged priority so that all sample handling and preservation takes place as rapidly as possible. Although no significant error has been reported for gas sensitive constituents pumped with a positive displacement bladder device when air is used as the drive gas, it may be prudent to switch the drive gas from air to N_2 at this point. Samples for dissolved gases are then taken, in-line ahead of the flow-through electrode cell at a flow rate of ~100 mL/min.

The samples for dissolved gases, volatile organic constituents, TOC and TOX are taken by carefully slowing the delivery rate to 100 mL/min or less and directing the flow to the bottom of the sample vessel (e.g. or by flowing into a syringe of appropriate volume) and allowing the vessel to overflow at least 1.5 volumes. The samples should be rapidly capped, excluding any headspace and preserved or put in the sample cooler as soon as possible. At this point, the time (and volume) of initial sample collection should be recorded. An effort should be made to keep track of the cumulative volume pumped during sampling and all subsequent steps. Samples for extractable organic compounds and total metals can then be collected. In filling the large volume bottles the

Table 3.5. Sample Purging Parameter Readings

Quantity pumped (liters)	pH	Conductivity Ω^{-1} ($\mu\int \cdot cm^{-1}$)
8	8.01	580
16	7.67	625
24	7.54	623
32	7.19	622
40	7.22	619
49	7.16	620
57	7.17	621
65	7.16	620

flow rate can be increased but should not exceed the pumping rate during purging.

At this point, the pump discharge is connected to an on-line filter apparatus and the samples for alkalinity, dissolved metals and other inorganic constituents can be collected in priority order. When the filtered samples have been collected, the time and cumulative volume pumped are recorded. One member of the sampling team should oversee the operation, insure proper preservation of the samples, and make the entries into the field and sampling logs of the time of sample collection, double-checking the labels on the storage vessels. Another member of the team should begin titrating alkalinity samples, at least in duplicate. The titrations should not be delayed more than two hours from the initial sampling time. The other member of the sampling team should be in charge of sample collection, time and volume measurements to insure that the samples and replicates are properly taken. Then the full flow is redirected through the electrode cell. Values of the well purging parameters should be recorded after the cell has been flushed at least once, if volume permits. These values should later be compared to those taken just prior to the collection of the initial samples to check on the stability of the water during the time of sampling.

Now the samples and field blanks should be properly preserved and stored. At least one replicate of each sample (excluding dissolved oxygen and alkalinity) should be spiked with an appropriate stock solution to provide a blind control standard for sensitive analytical determinations. To insure good quality control, these blind samples are labelled as an extra well and placed in the normal sample handling scheme enroute to the laboratory.

The gas supply to the pump is then turned off, and the pump with the tubing bundle can be retrieved. Before proceeding to the next well, the pump should be placed in a graduated cylinder of rinse or cleaning solution. The pump should be operated to detect any leakage and to clean the pump and the interior surfaces of the sampling train. Any waste water that may be contaminated with hazardous constituents should be managed in a responsible manner. Under no circumstances should it be returned to the well.

Field Determinations

The determination of alkalinity dissolved oxygenand other field constituents (e.g. pH, Eh, T and Ω^{-1}) should be completed at this point. Dissolved oxygen samples should be kept out of light, preserved and cold until the precipitate has formed and settled to the bottom of the bottle. After an hour or so, they should be shaken again and allowed to settle. So long as they are kept in the dark, they can be held for 4-8 hours prior to acidification and titration.

All other field parameters can be determined after method calibration has been performed, as conditions permit. At this time, the field and sampling logs should be checked for completeness and the initial chain of custody documentation has been completed.

Sample Storage and Transport

The procedures described in Section 2 should be followed explicitly from this point until delivery to the laboratory. Any unique circumstances (e.g. extreme heat or cold, delays in sample handling, etc.)

should be recorded in the field notebook. It is essential that the laboratory receive all information which may affect analytical processing. Notice of any extreme turbidity, reactivity with the preservation reagents, etc. should be provided in writing to the laboratory personnel.

These sampling procedures are sufficient to the needs of most ground-water sampling programs. If unusual conditions exist, they should be reported to the person in charge of the monitoring effort at once. This will help prevent undue exposure of sampling staff or water samples to conditions that may jeopardize health or the collection of high quality data.

SECTION 4
CONCLUSIONS

The development of reliable sampling protocols for ground-water quality monitoring is a complex, programmatic process that must be designed to meet the specific goals of the monitoring effort in question. The long-term goals and information needs of the monitoring program must first be thoroughly understood. Once these considerations have been identified, the many factors that can effect the results of chemical analyses from the monitoring program can be addressed.

In formulating the sampling protocol, the emphasis should be to collect hydrologic and chemical data that accurately represent *in situ* hydrologic and chemical conditions. With good quality assurance guidelines and quality control measures, the protocol should provide the needed data for successful management of the monitoring program at a high level of confidence. Straightforward techniques that minimize the disturbance of the subsurface and the samples at each step in the sampling effort should be given priority.

The planning of a monitoring program should be a staged effort designed to collect information during the exploratory or initial stages of the program. Information gained throughout the development of the program should be used for refining the preliminary program design. During all phases of protocol development, the long-term costs of producing the required hydrologic and chemical data should be kept in mind. These long-term costs are several orders of magnitude larger than the combined costs of planning, well construction, purchase of sampling and field equipment, and data collection start-up. It also should be remembered that high quality data cannot be obtained from a poorly conceived and implemented monitoring program, regardless of the added care and costs of sophisticated sampling and analytical procedures.

Finally, the ultimate costs of defending poor quality data in the legal arena or in compliance with regulatory requirements should not be overlooked. The damage to the credibility of the program can be substantial.

Due to the lack of documented standard techniques for developing monitoring programs, constructing monitoring wells, and collecting samples, quality control measures must be tailored for each individual site to be monitored. They should be designed to insure that disturbances to both the hydrogeologic system and the sample are minimized. The care exercised in well placement and construction, and sample collection and analysis can pay real dividends in the control of systematic errors. Repeated sampling and field measurements will further define the magnitude of random errors induced by field conditions and human error. Still the burden of assuring the success of a program relies on careful documentation and the performance of quality assurance audit procedures.

The hydrogeologic conditions at each site must be evaluated in terms of the potential impacts the setting will have on the design and effectiveness of the developed program. Documentation of the hydrology of the site is essential at the planning stage, as well as during the operational life of the program. Too little attention has been given to fully understanding the environment that is the source of water collected from monitoring wells. Only after the source of water is known (delineation of the vertical and horizontal components of ground-water movement) can the effectiveness of the program be assured.

The placement and construction of monitoring wells can be among the most difficult tasks involved in developing an effective monitoring program. The positioning of a monitoring point in a contaminant flow path must be determined on the basis of hydrologic data to insure that the well is capable of monitoring the contaminant plume or release. The monitoring wells also should be constructed using drilling techniques that avoid the disturbance of subsurface conditions due to the introduction of fluids or muds. Monitoring wells should be sized both to provide depth discrete hydrologic and chemical data and to maximize the usefulness of the collected data. The materials selected for monitoring well construction should be durable for the intended installation and minimize interference with the samples to be collected. The wells also should be properly developed to maximize their hydraulic efficiency and minimize the need to filter water samples.

Sampling mechanisms for the collection of ground-water samples are among the most error prone elements of monitoring programs. Documentation of the field performance for most devices and materials is lacking. Many of the sampling designs may be expected to provide adequate performance for conservative chemical constituents which are not affected by aeration, gas-exchange and degassing. Testimonials of sampling performance based on the recovery of conservative, unreactive chemical constituents are not reliable for planning effective monitoring efforts. It should be recognized that the purchase of a suitable sampler for most ground-water investigations is usually a very small portion of the overall program cost. It is further obvious that the choice of the right sampler made of appropriate materials will determine the ultimate usefulness of the chemical data. The recommended approach is to make the choice of both samplers and materials on the basis of the most sensitive chemical constituents of interest. Typically, reliable samples for dissolved gases, ferrous iron and volatile organic compounds are the most difficult to collect and handle.

The information needs of a ground-water monitoring program are determined by the stated goals of the program. They should be determined by the program manager, and field and laboratory personnel during the planning phase of the project. The long-term goals or anticipated needs of the program also should be addressed at the outset of the program to insure data consistency and quality throughout the life of the program.

The definition of a representative ground-water sample will vary from site to site and perhaps from sampling point to sampling point, depending on the situation under investigation. Performance criteria for the achievement of representative sampling should include the accuracy, precision, sensitivity and completeness necessary to provide a minimum level of confidence in the data. The criteria should be based on both knowledge of the system to be measured and the experience of the project planning staff. Close attention must be paid to the preliminary investigation, well placement and construction, hydrologic data, sampling frequency, and mobility and persistence of likely chemical contaminants. Natural or man-induced variability in the hydrogeology and geochemical characteristics of the site can only be distinguished from each other by the interpretation of high quality sampling results. It is hoped that by the careful implementation of the recommendations for sampling in this guide, that a level of confidence in ground-water data can be established. Our understanding of subsurface processes should improve in great measure as reliable investigations proceed.

SECTION 5

RECOMMENDATIONS

Well drilling/completion, purging, sampling and analysis steps all contribute to error in ground-water monitoring results. The procedures must be better understood as they effect particular classes of contaminants. This information is necessary in order to facilitate the development of efficient protocols and QA/QC programs. Specific problem areas which require further research include:

Drilling mud composition and effects on subsurface geochemistry.

Grouting materials and procedures which effectively seal screened intervals from leakage or cross-contamination, especially adverse effects of contaminants on grout set-up and integrity.

Well development procedures which are effective in reducing particulate matter in water samples.

Efficient methods for establishing monitoring points and sampling free-product or non-aqueous contaminant phases in the subsurface.

The effects of inadequate well-purging protocols prior to sampling for chemical analysis, emphasizing long term and short term well-casing material effects on sample integrity.

Once the most critical sources of error involved in specific contaminant monitoring situations have been identified, more basic studies of subsurface hydrogeology and sample handling must be done to minimize sources of systematic error and imprecision. Research is needed on:

Filtration effects on ground-water samples used for transport or contaminant flux investigations. The significance of total-recoverable (i.e., non-filtered) water sample analytical results for assessment work and colloidal transport effects require further investigation.

Methods for the interpretation of observed contaminant distributions in creviced or fractured geological materials and the unsaturated zone need improvement.

Improvements in geophysical monitoring methods and their relation to more traditional contaminant detection methods are needed.

One area that needs particular attention is the training of field and laboratory personnel in reliable monitoring techniques. The scientific literature on ground-water monitoring is developing rapidly. All monitoring personnel should make an effort to acquaint themselves with published materials and maintain a current understanding of advances in the field.

SECTION 5
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